GULF CANADA LIMITED

RESEARCH AND DEVELOPMENT DEPARTMENT

SHERIDAN PARK, ONTARIO, CANADA

IMPACT OF PROBLEMATIC COMPONENTS ON SYNTHETIC CRUDE PROCESSING

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1. INTRODUCTION

1.1 Objective

The primary objective of this project is to obtain background information on the nature of problematic components and their roles in processing heavy and synthetic feedstocks. A secondary objective is to define a possible new pretreatment process appropriate for facilitating upgrading residual oils.

1.2 Justification

The utilization of synthetic crude oils, when they become widely available, will be in the production of liquid transportation fuels. In conventional petroleum refining, a significant portion of these fuels are produced by converting residual oils into naphthas and middle distillates using catalytic processes. Since syncrude and other alternate feeds usually contain higher concentrations of metals, nitrogen, oxygen and sulfur, the economic feasibility of the catalytic processing is markedly affected by their presence. For instance, hydrocracking requires more severe hydrogen pretreatment due to the sensitivity of the hydrocracking catalyst to increased concentrations of nitrogen and sulfur compounds. In addition, metals such as vanadium, nickel and iron have deteriorating effects on catalyst life and promote undesirable side reactions.

Several pretreatment types are potentially available for improving economics of processing in fluid catalytic cracking or hydroprocesses. These pretreatments are anticipated to improve quality of catalytic cracker feed and maximize its output, while limiting coke laydown and metals buildup during secondary catalytic upgrading. The pretreatments involve a rejection of polar/carbon-high components and recovery of lighter, more processable material. Among many known processes, primary upgrading processes such as delayed coking and supercritical fluid extractions have been commercialized.

This study was launched to test alternative pretreatments based on the selective removal of specific types of the problematic components - the intent being to derive background information on the effect of feed compositional changes on catalytic processing.

Static extractions with aprotic dipolar solvents and extractions with supercritical fluids were chosen as techniques of selective removal of problematic components. Aprotic dipolar solvents, due to their highly polar nature and complexing affinities towards proton-donating species, offered a potential as extracting media. On the other hand, supercritical fluids were expected to promote unique selectivities while allowing high molecular weight substances to vaporize.

1.3 Literature Review

1.3.1 Problematic Components

Nonhydrocarbons such as nitrogen, oxygen and metallic species impart unfavourable characteristics to heavy ends of conventional and nonconventional origin. An assessment of the structural types and processability of these species in residual and synthetic oils is still a complex problem. These problematic components occur in samples which are themselves multifarious molecular mixtures that do not easily lend themselves to direct investigation. Heteroatom removal and hydrodemetalation are usually measured/ characterized in terms of differences in specific element content. A limited number of studies report correlations between processability of heavy ends and various molecular types of problematic components.

The technical literature contains many references to processes suitable for the hydrodesulfurization (HDS) of heavy oils and residua (1). A variety of commercially proven processes are available for converting high-sulfur feeds to low-sulfur products.

On the contrary, the yields of hydrodenitrogenation may vary widely for the catalytic hydrotreatment. Commercial operations suffer from an exposure of catlayst to nitrogen species and incompleteness of their removal due to catalyst fouling and poorer product quality, respectively. Nitrogen components occurring in synthetic crudes and heavy ends are neither equally responsible for catalyst poisoning nor equally susceptible to hydrodenitrogenation. For fluid catalytic cracking poisoning by polycyclic aromatic bases, such as quinolines and acridines was found to be extremely harmful, while other nitrogen bases behave similarly to hydrocarbons (2). The poisoning of a dealkylating catalyst by nitrogen compounds increased as follows: quinaldine > quinoline >

pyrrole > piperidine > decylamine > aniline (3). Some nitrogen components, such as species with pyrrolic groups, were found to be the least readily removed during hydrotreating (4).

Minute amounts of metals in the charging stocks for catalytic cracking influence the activity of the catalyst and result in increased gas and coke formations and reduced yields of gasoline. The catalysts generally deactivate in two steps. These are a rapid decline in activity due to coke formation, followed by a slow decline in activity due to metals deposition. Among many elements occurring in oil-soluble form, vanadium and nickel in particular deposit on the cracking catalyst, and even small concentrations in feeds eventually lead to significant deposits.

Two major classes of metal complexes are of primary importance: porphyrins and nonporphyrins. The difference between these two classes is based on the properties of isolated fractions i.e. structural types of ligands and susceptibility to demetalation (5). Different reactivities of metal complexes are strongly manifested during hydrotreating heavy and residual oils. Even severe hydrotreating may not completely remove the nickel and vanadium. In addition, differences in the chemical composition of coke deposits (6) imply that various types of nitrogen and oxygen ligands complexing with metals are responsible for different reaction pathways for the hydrodemetalation.

1.3.2 Solvent Extraction

A variety of extraction processes is available for maintaining concentrations of the asphaltic components in feeds at a minimum. The removal of the asphaltenes is aimed, in particular, in reducing the metals, sulfur and nitrogen contents in feedstocks destined for catalytic hydrotreatment. The processes are based on use of a light hydrocarbon solvent to precipitate the asphaltic constituents leaving a deasphalted oil that contains less sulfur, nitrogen, metals and high molecular weight aromatics than the feedstock. The propane deasphalting is most widely employed.

Solvent extraction has recently become inportant due to its potential in improving heavy and residual oil conversion. By using hydrocarbon solvents as supercritical fluids, a significant

advancement over conventional deasphalting in yield, product utilization and energy efficiency were reported (7,8). The oils demetallized in this manner were more easily processed in downstream catalytic units i.e. less severe conditions with much lower catalyst consumption were required than for residua.

1.3.3 Supercritical Fluids

The papers, reports and patents, which have appeared over the past few years, demonstrate an increased interest in supercritical fluids for extraction processes.

Serious consideration is now being given to fluid extractions in various industries, due to the selectivities achieved and energy economics offered in comparison to conventional distillation. Energy related applications include the extraction of coal with supercritical gases as a potential route for the production of liquid fuels (9-12) and supercritical extractions of petroleum residue for rejecting undesirable constituents (13).

The supercritical extraction technique is based on the ability of substances to vaporize in the presence of a compressed supercritical gas. Under favourable conditions the effect can be very large, and an increase in volatility up to 10,000 times can be obtained (9). This ability to vaporize low-volatile substances seems to be particularly useful for substances which decompose before reaching their boiling point and perhaps those involved in the irreversible process of resid formation. Extracts obtained by using supercritical fluids may contain materials that are usually not dissolved by common solvents. The term "destraction" has been coined for supercritical extraction, because the processes bear a similarity to both fractional distillation and extraction (14). Since there is a great lack of experimental data on the fluid extractions, factors operative and some practical remarks mentioned in various literature sources will be outlined below.

A supercritical fluid is a substance which has been raised to a temperature, called the critical temperature. Above this temperature a low density fluid (gas) can be compressed to high density fluid (liquidlike) without a discontinuity in density (i.e. without a gas to liquid condensation), regardless of the external pressure applied to the system.

The solubilizing power of a supercritical fluid is controlled by a large number of variables, particularly for dynamic (flow-through) systems. Both pressure and temperature influence the solvent power of a supercritical fluid (15). However, its density, which increases with pressure, is a better parameter to illustrate temperature dependence of such power. General rules valid for supercritical fluids have been postulated using supercritical carbon dioxide (16). These are:

i. solvent power of a supercritical solvent increases with density of a given temperature,
ii. solvent power of a supercritical solvent increases with temperature at a given density.

The effectiveness of supercritical extractions is dependent on the transport properties of the fluid. These properties include viscosity, solute diffusivity and thermal transport. The values of corresponding parameters for supercritical fluids are between those of liquid and gas. In general, supercritical fluids offer a favourable combination of properties. The fluids are solvents whose densities are high enough to allow good solubility, but transport properties begin to approach those of gases.

Some similarity between the supercritical extraction of coal and heavy ends was expected. The formation of pores in coal i.e. a physical access of extracting medium to coal components controls extraction yields. Our past work has indicated that the physical access of solvent to highly polymerized/condensed resid constituents might have been a factor limiting extraction yields. Thus, a postulate that the supercritical fluid attacks coal, breaking it down and removing the material (17), led us to believe that similar action may break the resid agglomerates. The supercritical extractions are expected to be influenced by other factors in addition to those operative for coal. They include: type and state of solvent, solvent to sample ratio, method of contacting phases and extraction time. Finally, it is worth mentioning that temperature may control the mechanisms of supercritical extraction. Such mechanisms have been distinguished for coal and include: physically controlled extraction yields and thermal decompositions (18,19).

Under supercritical conditions the physical properties of the solvents change. The changes in dielectric constant and electric

conductivity appear to influence the solubilizing power of supercritical solvents. The effects of pressure on the dielectric constant and selectivities induced were described in (15) and (20), respectively. Consequently, correlations between the yield of the supercritical extraction and the Hildebrand solubility parameter were also found to indicate the importance of the intrinsic properties of the fluid. The solubility parameter, varied by changing pressure and solvents, controlled the conversion of coal (21,22).

1.3.4 References

(1) J.G. Speight, "The Desulfurization of Heavy Oils and Residua" Marcel Dekker, Inc., New York 1982

(2) C.M. Fu and A.M. Schaffer, ACS, Div. Petr. Chem. Vol 28, No. 4 (1983) 876

(3) G.A. Mills, E.R. Boedeker and A.G. Oblad, JACS, 72 (1950) 1554

(4) S.A. Holmes and L.F. Thompson, Fuel 62 (1983) 709

(5) J.F. Branthaver, Thesis, Ann Arbor, Michigan; University Microfilms Inter. 1977, 76-28448

(6) E. Furimsky, Ind. Eng. Chem. Prod Res. Dev. 17 (1978) 329

(7) J.A. Gearhart, Hydrocarbon Processing 59 (May 1980) 150

(8) R.T. Penning, A.G. Vickers and B.R. Shah, Hydrocarbon Processing, May 1982, 145

(9) J.C. Whitehead and D.F. Williams, J. Inst. Fuel 48 (1975) 182

(10) R.R. Maddocks and J. Gibson, Chem. Eng. Prog., 73(6) (1977) 59

(11) R.R. Maddocks et al., Chem. Eng. Prog., 75(6) (1979) 49

(12) K.D. Bartle, et al., Fuel 54 (1975) 225; 58 (1979) 412; 58 (1979) 423

(13) Kerr-McGee Refining Corp., Chem. Eng. 88(24) (1981) 69

(14) T.P. Zhuze, Petroleum (London) 23 (1960) 298

(15) G. M. Schneider, Angew. Chem. Int. Ed. Engl. 17 (1978) 716

(16) H. Brogle, Chem. and Ind., 19 June 1982, 385

(17) J.C. Fetzer, et al., Sepn. Sci. and Tech. 16 (1981) 97

(18) B. Slomka and A. Rutkowski, Fuel Process. Tech. 5 (1982) 247

(19) B. Slomka, A. Rutkowski and M. Liszka, Fuel Process. Tech. 7 (1983) 71

(20) T.J. Gouw and R.E. Jenoft, "Chromatography in Petroleum Analysis", Marcel Dekker, Inc., New York, 1979, p 313

(21) J. Jezko et al., Fuel Process. Technol. 5 (1982) 229

(22) J.R. Kershaw, Fuel Process. Technol. 5 (1982) 241

2. EXPERIMENTAL (Methodology and Data)

2.1 Samples

The samples were either prepared from the crudes supplied or used as obtained from the operating departments of Gulf Canada. The exception was Suncor raw coker gas oil obtained from Alberta Research Council. Information on the samples employed in the project is compiled in Table 1.

2.2 Static Extractions

PROCEDURE A

The samples and equal quantities of each individual solvent were stored at temperatures slightly below the boiling points of the solvents for a minimum of 24 h, shaken occasionally and sonicated at elevated temperatures for 1-2 h. Then the mixtures were centrifuged and the two phases separated. The extracts were recovered after evaporation of the solvent. The extraction yields and contents of nitrogen, vanadium and nickel are reported in Table 2. The corresponding distributions of the nitrogen species between raffinates and extracts are shown in Table 3.

PROCEDURE B

The samples, whose extractions were feasible using procedure A, were refluxed with equal amounts of individual solvents - acetone, nitromethane and pure DMSO. Then, the mixtures were transferred into separatory funnels and stored overnight in the oven at the stirring temperatures. The disengaging phases were observed under UV light. However, due to incomplete disengagement, only small amounts of the extracts were obtained.

The NH and -OH contents of the extracts, which were nonquantitatively recovered are shown in Table 4. Analyses for vanadium and nickel are shown in Table 5.

PROCEDURE C

The heavy ends were dissolved in a heavy straight run distillate (195°C) of the following composition: paraffins 43.0%, cycloparaffins 46.1% and aromatics 10.9%. Aprotic dipolar solvents were added to the solutions of heavy ends in a ratio of 1:1. Then the mixtures were sonicated for 2 hours and centrifuged for 30 minutes at 12,000 rpm.

Table 6 reports on the extraction yields. The nitrogen and metals contents in the corresponding raffinates are shown in Table 7.

PROCEDURE D

The samples and equal quantity of DMSO containing water were shaken for 2 h, and left overnight at room temperature to disengage. Then the phases were separated. The extracting medium was distilled off under vacuum at 160°C from extractees and raffinates. The extraction yields and nitrogen distributions are shown in Tables 8 and 9.

The procedure 'D' was also employed for the 2nd stage extractions with DMSO containing acid. The denitrogenations observed are shown in Tables 10 and 11. In addition, the extractions with alternate solvents were performed using the same procedure and sample to extractant ratio 1:1 (Tables 12 and 13). The nitrogen contents of the extracts and their nonbasic subfraction are reported in Table 14.

2.3 Supercritical Fluid Extractions

The extractions were carried out using 1 L or 2 L autoclaves and remotely actuated sampling cylinders. A sketch of the facility and typical experimental procedure are attached - Figure 1 and Appendix 1, respectively. The extractions with acetone, acetic acid and methanol were performed using a 2 L autoclave, while sulfur dioxide and water employed the 1 L vessel. In addition, the facility for SO_2 extractions was equipped with a blowdown tank for retaining charged SO_2 in emergency situations and with a scrubber for disposing SO_2 after finishing the experiments. The experimental conditions employed and extraction yields obtained are shown in Tables 15-19, while analyses are reported in Tables 20-23.

2.4 Characterization Methods

INFRARED SPECTROSCOPY

Solutions of approximately 1 g of sample in 50 mL of CCl_4 were prepared. The IR spectra of feeds, raffinates and extracts were taken using the dispersive IR spectrometer (Perkin Elmer 283B). The pyrrolic NH and alcoholic -OH content were determined using carbazole and sitosterol as a calibration standard respectively.

CHROMATOGRAPHY

The high performance liquid chromatograph (HPLC) system (Series 8800) from DuPont (Wilmington, DE) consisting of a gradient controller, pump, UV spectrometer, and column compartment equipped with Rheodyne injection valve was used. Analytical and semi-preparative scale separations were performed employing system described elsewhere (J. Chmielowiec, Anal. Chem. 55 (1983) 2367). A 250 x 4.6 mm silica (Partsil, 10 m) column from Whatman, Inc. (Clifton NJ) and 25 x 0.94 cm silica (Spherisorb, 5 m) column from CSC, Inc. (Quebec, Que.) columns were used, respectively. HPLC grade CCl_4 was stored over sodium hydroxide and filtered through basic alumina before use.

MASS SPECTROMETRY

Mass spectrometric analyses were performed on selected extract samples using high resolution instrument Model 902 from Kratos, Manchester, England. The samples were analyzed for compound type. The approximate percentages of groups, such as CH, S, O, N, NS, NO and SO were determined.

The spectrometer was used at a resolution of approx. 10 000 and the ion source was operated at an electron beam energy of 57 eV and a temperature of 245°C. Three microlitres of sample and one microlitre of a reference material (perfluorokerosene) were introduced through an all glass heated inlet system. Several scans of the spectrum were collected by a dedicated DG NOVA 3 computer and an appropriate scan was selected for further processing. The sample peaks were summated according to group

types. The mass % of each group type was determined by a matrix solution of the summations using a 36 x 36 matrix developed in-house.

DETERMINATION OF TRACE METALS

A routine atomic absorption method was used for determining trace metals. A sample was reacted with dodecylbenzene sulfonic acid and ashed. The residue was dissolved in dilute hydrochloric acid. A nitrous oxide - acetylene flame was used for determination of nickel and vanadium.

DETERMINATION OF THE SULFUR CONTENT

A routine method based on ASTM 1552 was employed using LECO Analyzer.

DETERMINATION OF THE NITROGEN CONTENT

The nitrogen contents of SSC ATB, SUC GO, IPL ATB and their raffinates were determined measuring chemiluminescence of nitric oxide as described elsewhere (H.V. Drushel, Anal. Chem. 49 (1977) 932). The Antek Nitrogen Detector (Antek Instruments, Inc. from Houston, Texas) was used. The nitrogen content of the other heavy ends was determined by Kjeldhal method (ASTM 3228).

2.5 Microactivity Test (MAT)

The laboratory sized MAT unit designed to simulate the performance of a cracker feed in a full sized catalytic cracking unit was used. Microactivity tests were carried out to correlate the selective removal of problematic components with feed processability.

The procedure employed was based on ASTM D3907-80 which is a standard method evaluating FCCU catalyst activity. A schematic diagram of the experimental apparatus is shown in Figure 2. A MAT reactor was a 40 cm long x 1.2 cm O.D. tubular reactor packed with known amount of catalyst DA-250 from Davidson, Baltimore. The feedstocks were injected onto the catalyst bed in amounts of approximately 1 mL of equilibrium temperature. The products: gases, liquids and coke on spent catalyst were determined for calculating a complete product yield. The derived data were fed to a reduction program to calculate the conversion and yield structure.

Since the directly determined weights of products do not necessarily equal the weight of feed, MAT product yields are made whole by assuming any discrepancies in the data are due to errors in the amount of gas determined. This results in the weight of gas being corrected in order to force a mass balance, and therefore the relative amounts of each of the gas components are adjusted accordingly. Gasoline yields are calculated from the C_5^+ gasoline components and the weight of reactor effluent liquid which boils up to 220°C. Cycle oil yields are calculated directly from gas chromatographic distillation data and the weight of reactor effluent. This data is all reported on a mass % basis which is atypical with most of the data reported in the literature, particularly that from commercial operations which is reported in liquid volume %. Due to the very small samples of materials collected and the fact that they are not fractionated into products, densities cannot be measured and accurate volumetric yields reported. However, the data can be converted to such yields if one is willing to assume average specific gravities for various materials. This should be done with caution.

The product yields are reported as a mass % of the feed and were calculated with the following expression:

$$\text{yield ith product} = (\text{weight ith product}/\text{weight feed}) \times 100$$

3. RESULTS AND DISCUSSION

3.1 Static Extractions

Three aprotic dipolar solvents: acetone, nitromethane and dimethylsulfoxide were initially used in the extraction experiments on eight samples of heavy ends. The objectives of the extractions were identifying compositions of extracting media and developing methodology for performing effective and efficient extractions. Consequently, selective removal of polar and/or metallic species and disengaging phases in short period of time were expected, respectively. Primarily, the raffinates and extracts were investigated for distributions of nitrogen and metals as well as extraction yields were monitored. The low yields were desirable from the practicality standpoint.

Several extractions employing procedure 'A' yielded nitrogen-rich extracts, while the extractions on five heavier samples were not feasible (Table 2). The lowest extraction yields were observed for nitromethane and DMSO containing water. The latter, however, was superior denitrogenating agent (Table 3).

The extracts obtained using acetone, nitromethane and DMSO/H_2O (96:4) contained polar species. The chromatograms (Figures 3-5) show relative differences in contents of the polars as intensities of the second peak as well as second and third peaks for IPL VTB increase from the lowest for acetone extract to highest for one obtained with DMSO/H_2O (96:4). The semi-preparative chromatography of the IPL extracts followed by mass spectrometric characterization (Table 2A) showed that the extract obtained with DMSO/H_2O (96:4) contained significantly less hydrocarbons than the acetone extract. In addition, the nitrogen constituents of the former comprised higher aromatic ring structures. A comparison of three types of extracts from SCC ATB (Table 2B) also revealed the most favourable transfer of nitrogen compounds and greatest affinity to polynuclear aromatic hydrocarbons (PAHs) for the DSMO based extracting medium. The corresponding distributions of extracted component types are shown in Figure 6. Parallel examinations of the extracts by means of IR spectroscopy provided an evidence on the presence of NH type constituents characterized by HRMS as nitrogen containing compounds with 'Z' number ranging from -15N to -21N. These were tentatively identified as carbazoles and benzocarbazoles. Since IR spectra of all the samples

showed distinct absorbance at 3480 cm^{-1}, the absorptivity at this frequency was measured for determining the NH content. Samples produced in the extractions to follow were analyzed for the NH content using carbazole as a calibration standard. Typical spectra obtained for untreated SCC ATB and its raffinate are shown in Figure 7.

The extractions employing procedure 'B' involved samples of the non conventional heavy ends and resulted in poorly disengaged phases noticeable only under UV light. The recovered solvent phases yielded small amounts of extracts high in NH and OH species (Table 4). There was no enrichment in metals (Table 5). In addition, poor solvent recovery and nonquantitative disengagement of the extracting medium did not permit determining actual distributions of nitrogen, oxygen and metallic species.

In order to improve disengaging phases and their contact, samples of the non-conventional heavy ends were dissolved in naphtha (HSRD) and then extracted using procedure 'C'. Both increased extraction yields and selective transfer of nitrogen species into the DMSO phase were observed for extractions employing pure DMSO (Tables 6 and 7). Infrared spectra of extracts obtained with N-methyl formamide did not show any enrichment in NH and/or OH constituents. In general, the procedure 'C' proved feasibility of extracting nitrogen species from nonconventional heavy ends.

Based on the results of the above scouting experiments DMSO was chosen as potentially the most desirable solvent for selective extracting nitrogen species. Because of the project time frame, extractions solely on three lighter feeds were continued. These feeds were: SSC ATB, SUC GO and IPL ATB. The objective of the concluding series of denitrogenations was maximizing selective nitrogen removal while tailoring DMSO/H_2O phase composition to minimize extraction yields. Since repeatable results were obtained for three lighter feeds using less time-consuming procedure 'D", the extractions to follow employed this procedure.

The extractions with DMSO containing water in increasing amounts are reported in Tables 18 and 9. The increasing water content was found to diminish both the overall nitrogen transfer and extraction yield. The extraction selectivity was also influenced by varying water content.

Values of the partition ratios, k_{z_i}, indicated more preferential transfer of the NH type components into the extracting medium for lower water contents. On the other hand the extractant capacity was significantly lower for higher water contents. The tabulated nitrogen contents were used for determining values of a selectivity factor defined as follows:

$$S_{NH/N} = K_{NH}/K_{Total\ N} =$$

$$= \frac{M^E_{NH} \cdot M^R_{Total\ N}}{M^R_{NH} \cdot M^E_{Total\ N}} = \frac{C^E_{NH} \cdot C^R_{Total\ N}}{C^R_{NH} \cdot C^L_{Total\ N}} = \frac{DF^E \cdot DF^R}{DF^R \cdot DF^E} = \frac{C^E_{NH} \cdot C^R_{Total\ N}}{C^R_{NH} \cdot C^E_{Total\ N}}$$

where K_{z_i} = distribution coefficient

$M^E_{z_i}$ = concentration of the z_i compound type in the extractant

$M^R_{z_i}$ = concentration of the z_i compound type in the raffinate

$C^E_{z_i}$, $C^R_{z_i}$ = nitrogen contents of the z_i compound type in the lower and upper phase, respectively

DF^E, DF^R = dilution factors

Values of the selectivity factors decreased with increasing water content (Figure 8). Such decrease implied lower selectivity of the removal of the NH component type and led either to complete lack of the selectivity (S=1) or its reversal (S<1). The selectivity reversal was observed for two stage extractions of SSC ATB. This has led us to believe that there is a capability of tailoring composition of the extractant to extract nitrogen species without noticeable preference between basic and nonbasic nitrogen components.

An extraction efficiency was assessed by determining a denitrogenation coefficient which was defined as a ratio of amount of nitrogen removed, wt%, to amount of feed removed, wt%. Values of the denitrogenation coefficient were found to increase with increasing water content (Figures 9 and 10). In particular, the two stage extractions seemed to yield relatively the most effective denitrogenations.

An imcomplete solvent recovery from the raffinate phase was observed. The solvent stayed in this phase and its removal was incomplete when distilling at 160°C under vacuum. The DMSO content was assessed indirectly from nitrogen contents determined for the raffinate samples before and after stripping with water. It was found that the 1st stage raffinates contained DMSO approximately in amounts as follows: SUC GO 1.5 wt%, SSC ATB 2.4 wt% and IPL ATB 9.2 wt%.

To enhance the denitrogenations, 2nd stage extractions with DMSO containing acid and 1st stage extractions with aprotic dipolar solvents were carried out. Denitrogenations observed due to the presence of acids are reported in Tables 10 and 11. The maximum denitrogenation was achieved for 6% of 10N H_2SO_4 in DMSO. The extractions with DMF and NMP (Tables 12 and 13, respectively) were less effective than those with DMSO, because they involved higher extraction yields. However, both solvents permitted significant denitrogenations. The 2nd stage extractions with DMSO/H_2O (94:6) on the 1st stage raffinates obtained with DMF/H_2O (9:1) and NMP/H_2O (9:1) showed that the former agent was a more efficient extractant than the latter media.

Extracts obtained with DMSO/H_2O (94:6) were analyzed for the nitrogen content (Table 14). The SSC ATB extract was the most abundant in nitrogen species. Re-extractions of the basic nitrogen compounds from the extracts decreased their total nitrogen content and led to increased ratios of nonbasic (pyrrolic) nitrogen content to total nitrogen content. Liquid chromatographic separation of the nonbasic fraction on the clay column preconcentrated nonbasic nitrogen compounds even more. Nitrogen contents of the nonpolar- (predominantly hydrocarbon-) and highly polar-subfractions are shown in Table 14A. The polar subfractions contained pyrrolic-type components. However, due to the poor

sample recoveries from the clay column, general characteristics/ structures of all the nitrogen extractees could not be obtained. An assignment of the tentative structures requires complete sample recovery prior to molecular characterization.

3.2 Supercritical Extractions

Five polar solvents were used as supercritical fluids to perform extractions. These solvents were: acetone, acetic acid, methanol, sulfur dioxide and water.

Acetone Fluid

Six feeds were treated with acetone fluid (Table 15). The extract samples analyzed by gas chromatographic distillation and HRMS revealed that gas oil range hydrocarbons were extracted. In addition, the extracts contained small amounts of mesityl oxide - apparently from conversion of acetone. The contents of nitrogen, vanadium and nickel in the extracts were below those of untreated samples. The transfer of NH species into the acetone phase was also less selective than that at ambient conditions. In general, supercritical acetone offered affinities towards preferential interactions with hydrocarbons. The analyses of the extracts and raffinates are shown in Table 20.

Methanol and Acetic Acid Fluids

The experimental conditions and extractions yields for experiments employing supercritical acetic acid and methanol are reported in Tables 16 and 17, respectively. Table 21 reports analyses performed on the extracts and raffinates. Only selected samples were analyzed for nitrogen and metals. Due to the non-selective nature of these above scouting experiments, the extractions employing other feeds and analyses of the balance of the samples were not performed. Based on the high concentrations of nickel in the extracts and raffinates, it was concluded that both fluids were leaching Ni from the autoclave walls or other parts.

Sulfur Dioxide Fluid

Ten experiments were carried out with sulfur dioxide (Table 18). The extractions performed on AB ATB and LHO VTB at temperatures <200°C yielded solid products (coke-like). The solids were only slightly soluble in toluene and methylene chloride. The solid

product from AB ATB was higher in sulfur (29.2% of S for methylene chloride insolubles and 33.6% of S for toluene insolubles) than that from LHO VTB (24.4% of S for methylene chloride insolubles). Both solids contained several times more sulfur than feed.

Next five experiments were performed under lower temperatures and reduced pressures. There was no coking effect observed. However. extraction yields were very low. Last three experiments were carried out under supercritical conditions. The solid product was obtained only in the experiment No. 9. The extractions Nos. 8 and 10 employing lighter feeds and slightly lower temperatures and pressures did not produce solid products similar to those obtained in the experiments 1, 2 and 9. Due to the small quantities of extracts available for characterization, only a limited number of analyses were performed (Table 22). These indicated lack of selectivity for nitrogen species.

Water Fluid

Higher extraction yields were obtained for water than other polar solvents (Table 19). Based on the summary of analyses performed (Table 23), the extractions were found to be nonselective with respect to nitrogen and vanadium. High concentrations of nickel were observed in all the VTB's and ATB's of AB and LHO. In addition, the examinations by IR spectroscopy revealed strong absorption bands in the carbonyl vibrations range. It was concluded that nickel had been leached from the vessel walls and carbonyl absorbance coming probably from nickel carbonyl.

3.3 FCC Microactivity Tests

The fluid catalytic cracking microactivity tests permit determining conversion and structure of product yields. Here, the MAT was used to correlate raffinate processability with selective removal of nitrogen constituents from SSC ATB, IPL ATB and SUC GO.

The MAT product yields for SSC ATB raffinates (Table 24 and Fig. 12) show that the decreased nitrogen content may have been responsible for their changed FCC processability. An increased yield of C_5+ gasoline, approximately 4 wt%, seemed to correspond to denitrogenations with DMSO containing 2 or 6% of H_2O. The raffinates obtained with phases containing more water produced

less C_5^+ gasoline. However, MAT results for the 2nd stage raffinate obtained using 15% of H_2O in DMSO revealed a potential of multistage extractions with high water content medium. Such extractions are expected to lead to high degree raffinate conversion into light liquid products, while removing lesser amounts of the extraction feed, than one stage treatments with low water content extractant. A comparison of the product yields of raffinate washed with water with those of raffinates with incompletely recovered DMSO indicated that stripping DMSO might lead to lower yields of gases. The extractions with NMP, which appeared also to be an effective denitrogenation agent, were found to benefit raffinate processability by increasing C_5^+ gasoline yield and decreasing coke lay-down.

The 2nd stage raffinates, denitrogenated to a higher degree by using DMSO-containing acid, showed different cracking behaviour than those treated only with DMSO-containing water (Table 25 and Figure 13). An increase in gasoline yield up to 5 wt% and decrease in coke yield, except for the raffinate not stripped with water, were observed. In general, the 2nd stage extractions with extractants containing acid were found to be beneficial for improving processability of SSC ATB. Consequently, the increased denitrogenations appeared to contribute to increased C_5^+ gasoline yield.

A complementary evidence on the relationship between nitrogen compounds and raffinate processability was provided from MAT results for reconstituted SSC ATB's (Table 26 and Figure 14). The reconstitutions were achieved by recombining raffinate with extract, its fraction, or by adding model nitrogen compounds in ratios corresponding to the pre-extraction nitrogen content (1621 ppm). The reconstitution with extract resulted in very close yields of gases, C_5^+ gasoline and coke, Recombining raffinate with a nonbasic fraction of the extract i.e. fraction with increased NH content showed significantly lower yields of gasoline and gas products. The addition of 13H-Dibenzo(a,i)carbazole and/or acridine resulted in close yields of C_5^+ gasoline, and in contrast higher coke and gas yields. 7,8-Benzoquinoline was found to be the strongest catalyst poison reducing considerably total conversion and yields of gas, coke and gasoline.

The extractions carried out on IPL ATB and SUC GO, which were followed by MATs, confirmed trends identified for SSC ATB (Tables 27, 28 and Figure 15). These were: increased yields of C_5+ gasoline (up to 6 wt%) and importance of stripping DMSO with water. An increased yield of C_5+ gasoline was observed for NMP raffinate of IPL ATB, while DMF increased this yield to a lesser extent. Both alternate solvents decreased coke lay-downs. Due to the limited number of MATs performed on both feeds and their raffinates, and consequently insufficient data base, four micro-activity tests yielding unexpectedly low or too high conversions are neither reported nor discussed here.

4. CONCLUSIONS AND RECOMMENDATIONS

4.1 Static Extractions

A selective extraction concept based on the use of aprotic dipolar solvents was experimentally demonstrated and verified. Species containing nitrogen were selectively removed from various feeds. These solvent treatments, which were found to be more effective for lighter feeds, decreased the nitrogen content up to 75%, while removing several percentage fractions of the samples treated.

A relationship between the FCC processability and nitrogen constituents became apparent from this research study. The pretreatments were found to increase the gasoline yields up to 6 wt%, while lower coke yields were observed.

Future work should concentrate on:

- applicability of extractions to other feed types;
- assessing pretreatment employing NMP and DMF based-phases for selectivity of nitrogen removal, denitrogenation effectiveness and MAT product yields;
- determining optimum composition of the DMSO based phase for multistage extraction;
- studying effect of temperature on the selectivity extractions and denitrogenation;
- advancing characterization of extractees.

An overall objective of the future work should be maximizing conversion to light liquid product, while a consideration should be given to improving practicality of the pretreatments reported.

4.2 Supercritical Extractions

A selective removal of problematic components such as nitrogen compounds and metal-containing species from heavy ends was not observed. The pretreatments proveed feasibility of performing supercritical extractions on heavy ends with polar solvents i.e. equilibrium conditions were easily maintained and phases disengaged quickly. Since supercritical fluids offer a favourable combination of properties, "trial and error" extractions employing potentially selective extractants should be continued.

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TABLE 1

Samples Studied

Crude	Source and/or History	Samples prepared or obtained
Athabasca Bitumen (ATB)	Syncrude Plant Site - Hot Water process	ATB fraction (360°C+) VTB fraction (504°C+)
Lloydminster Heavy Oil (LHO)	Primary production Well A15-24-47-27 W/3	ATB fraction (360°C+) VTB fraction (495°C+))
Interprovincial Pipeline Crude (IPL)	Gulf Refinery in Clarkson - Samples taken February 28, 1983	ATB fraction (360°C+) VTB fraction (524C+)
Syncrude Synthetic Crude (SSC)	Edmonton-Fort McMurray pipeline - Samples taken February 27, 1983	ATB fraction (385°C+)
Suncor Untreated Crude (SUC)	Sample obtained from Alberta Research Council	Raw coker gas oil

TABLE 2

Extraction Yields and Contents of N, V and Ni (Procedure 'A')

Sample	Untreated Sample N ppm	V ppm	Ni ppm	DMSO/H_2O (96:4) Raffinate N ppm	V ppm	Ni ppm	% Fraction Removed	Nitromethane Raffinate N ppm	V ppm	Ni ppm	% Fraction Removed	Acetone Raffinate N ppm	V ppm	Ni ppm	% Fraction Removed
IPL ATB	380			190			1.2	400			2.3	180			52.7
IPL VTB	4450	34.3	18.0	4380	27.1	19.8	0.67	4630	34.4	20.2	0.56	4060	29.9	18.9	16.7
SSC ATB	1621			829			4.9	1260			4.8	1066			33.9
SUC Gas Oil	2017	1.3	<0.2	1124	2.1	0.2	15.5	1874	2.5	0.6	4.1	one phase mixture			
LHO ATB	4051	173	60	3984	162	49.4	18.1*	4339	169	50	16.0*	not feasible			
LHO VTB	Static extractions were not feasible using procedure A due														
AB ATB															
AB ATB	to poor phase contact and poorly disengaged phases.														

* Yields are too high due to difficulties in solvent removal.

TABLE 2A

High Resolution Mass Spectrometry of the Extracts

Sample	Subfraction	Compound types (approx. mass %) HC	S	O	N	NS	NO	SO	Comments
Acetone extract of IPL VTB	1								Sample contains approx. 30% unresolved nitrogen compounds and 70% hydrocarbons (predominantly polynuclear aromatics).
	2	0	0-5	0-5	70-75	10-15	10-15	0	3-5 ring nitrogen compounds
	3	0	5-10	0	45-50	5-10	30-35	0	5-6 ring nitrogen compounds; NO compounds - approx. 1/3 amides; most of N compounds neutral.
	4								Spectra characteristics for high O-compounds sample - IR analysis may give more information.
	5								
DMSO extract of IPL VTB	1	5-10	0-5	5-10	80-90		0	0	The pure hydrocarbon compounds are 6-7 ring structures; N & NS compounds are mostly 4-6 ring compounds.
	2	0	0	0	60-70	5-10	20-30		The pure nitrogen compounds are mostly 6-7 ring structures.
	3	0	10-15	0	20-25	0	65-70	0	The NO compounds are mostly 6-7 ring structures.
	4								Spectra characteristic for high O-compounds sample - IR analysis may give more information.
	5								

TABLE 2B

High Resolution Mass Spectrometry of Syncrude Samples (Mass%)

Component Types	Syncrude 385°C+	Acetone Extract	Acetone Raffinate	Nitromethane Extract	Nitromethane Raffinate	DMSO Extract	DMSO Raffinate
	Samples						
Paraffins	4.0	2.4	6.3	1.2	4.5	0.5	4.4
Cycloparaffins	33.3	25.0	42.9	13.7	36.9	3.8	36.6
Monoaromatics	19.8	18.0	18.2	11.8	19.4	2.8	19.6
Diaromatiacs	15.5	18.4	12.8	20.0	15.0	17.5	14.9
Triaromatics	11.8 ≅3%	16.5 ≅3%	9.5 1-2%	24.8 ≅10%	11.0 20-3%	32.9 ≅15%	11.2 ≅2%
Tetraaromatics	7.5 N-com-	10.2 N-com-	5.1 N-com-	15.9 N-com-	6.2 N-com-	24.9 N-com-	6.2 N-com-
Pentaaromatics	3.9 pounds	4.6 pounds	2.6 pounds	5.6 pounds	3.3 pounds	7.3 pounds	3.5 pounds
Polyaromatics	0.1	0.2	0.0	0.2	0.2	0.5	0.2
Thiophenes	3.0	4.1	2.0	6.1	2.5	9.0	2.7
Furans	1.0	0.6	0.6	0.7	0.8	0.8	0.7
Nitrogen Compounds	from Z-15N to Z-23N; mostly carbazoles Z-15N	from Z-13N to Z-23N; mostly carbazoles Z-15N	from Z-13N to Z-19N; mostly carbazoles Z-15N	from Z-13N to Z-23N; mostly carbazoles and benzo-carbazoles (Z-15N and Z-21N, respectively)	from Z-15N to Z-23N; mostly carbazoles Z-15N	from Z-13N to Z-23N; mostly carbazoles and benzo-carbazoles (Z-15N and Z-21N, respectively)	from Z-15N to Z-17N mostly carbazoles Z-15N
Oxygen Compounds		Sample also contains ≅1% oxygen compounds (Z-6 O to Z-12 O)		Sample also contains ≅1% oxygen compounds (Z-6 O to Z-12 O)		Sample also contains ≅2% oxygen compounds (Z-6 O to Z-12 O)	

TABLE 3

The Nitrogen Content (N_{ppm}) of Extracts and Corresponding Raffinates

		Acetone Raffinate	Acetone Extract	Nitromethane Raffinate	Nitromethane Extract	DMSO/H_2O (96:4) Raffinate	DMSO/H_2O (96:4) Extract	Sample before Extraction
Syncrude 385°C+	NH	478	1525	546	6132	355	10 810	855
	Total N	1066	2670	1260	7040	829	12 570	1621
Suncor Coker Gas Oil	NH	homogeneous solution		406	3390	161	2209	592
	Total N			1874	6197	1124	5599	2017
IPL ATB	NH	58	549	56	4390	28	9113	166
	Total N	180	(559)*	400	6102	190	(15 201)*	380

NOTE: Carbazole was used as a calibration standard for determining NH species by IR spectroscopy

* Calculated nitrogen contents

TABLE 4

Infrared Analyses of Alcohols and Pyrrolic-type Species
in Extracts Obtained by Aprotic Dipolar Solvents (Procedure 'B')

	LHO	ATB	LHO	VTB		AB	ATB		AB	VTB	
	Untreated Fraction	DMSO Extract	Untreated Fraction	DMSO Extract	CH_3NO_2 Extract	Untreated Fraction	DMSO Extract	CH_3NO_2 Extract	Untreated Fraction	DMSO Extract	CH_3NO_2 Extract
>NH (%)	0.60	2.63	0.78	2.43	1.46	0.73	3.32	2.07	0.82	2.81	3.71
-OH (%)	2.24	8.21	2.44	5.51	3.24	3.73	7.07	3.52	5.15	6.48	6.32

>NH measured at 3480 cm^{-1} - carbazole as a calibration standard

-OH measured at 3620 cm^{-1} (nonbonded phenolic and/or alcoholic functionality) - sitosterol as a calibration standard

TABLE 5

Metal Contents of Extracts Obtained Using Procedure 'B'

Sample	Untreated AB VTB	DMSO Extract	Nitromethane Extract
V ppm	275	283	321
Ni ppm	86.8	71.4	84.8

TABLE 6

Extractions of Bitumen with Selective Solvent Systems (Procedure 'C')

Sample	Sample Wt	% Extract	% Raffinate	Solvents
AB ATB	40.1 g	18.2	81.8	HSRD, DMSO
LHO ATB	40.3	19.1	80.9	HSRD, DMSO
LHO ATB	45.5	8.8	91.2	HSRD, 10% H_2O in DMSO
LHO ATB	40.3	14.8	85.2	HSRD, 5% H_2O in DMSO
LHO ATB	41.1	9.8	90.2	HSRD, 5% H_2O in DMSO
AB VTB	38.95	16.4	83.6	HSRD, DMSO
LHO VTB	38.80	24.1	75.9	HSRD, DMSO
LHO VTB	39.15	0.5	95.5	HSRD, 5% in DMSO
LHO VTB	41.70	1.6	98.4	HSRD, NMF
AB ATB	40.8	26.8	73.2	DMSO
AB ATB	37.07	5.15	94.85	HSRD, NMF
AB VTB	40.56	5.92	94.08	CCl_4, NMF
LHO VTB	41.70	1.56	98.44	HSRD, NMF
LHO AB	39.55	0.43	99.57	HSRD, NMF
AB VTB	42.3	37.3	62.7	HSRD, DMSO

Solvents Used: HSRD = heavy straight run distillate (naphtha)
DMSO = Dimethyl Sulfoxide
CCl_4 = Carbon Tetrachloride
NMF = N-methyl Formamide

TABLE 7

Analyses of Extracts and Raffinates Obtained Using Procedure 'C'

Sample	Solvents	N_{Total} (ppm)	N_{NH} (N ppm)	V (ppm)	Ni (ppm)
AB ATB	untreated	4010	608	198	84
AB ATB raffinate	HSRD, DMSO	4470	270	228	60.4
AB ATB extract	HSRD, DMSO	—	3960	261	59.2
AB ATB raffinate	HSRD, DMSO/H_2O (95:5)	—	340	130	63
AB ATB extract	HSRD, DMSO/H_2O (95:5)	—	1180	261	86
AB VTB	untreated	5550	691	264	89
AB VTB raffinate	HSRD, DMSO	4600		261	59.2
AB VTB extract	HSRD, DMSO			242	86
LHO ATB	untreated	4140	502	158	68
LHO ATB raffinate	HSRD, DMSO				
LHO ATB extract	HSRD, DMSO			157	56
LHO ATB raffinate	HSRD, DMSO/H_2O (95:5)	3910	300	130	63
LHO ATB extract	HSRD, DMSO/H_2O (95:5)		610		
LHO ATB raffinate	HSRD, DMSO/H_2O (1:1)		260	117	58
LHO ATB extract	HSRD, DMSO/H_2O (1:1)		540		
LHO VTB	untreated	5380	651	243	95
LHO VTB raffinate	HSRD, DMSO	4260		153	78
LHO VTB extract	HSRD, DMSO		410	226	82
LHO VTB extract	CCl_4, DMF		1150		
LHO VTB extract	DMF		660		

TABLE 8

Extractions with Dimethylsulfoxide Containing Water

Sample	Untreated Sample		RAFFINATES											
			Pure DMSO			2% H_2O in DMSO			6% H_2O in DMSO			10% H_2O in DMSO		
	NH (ppm N)	Total N (ppm)	% sample removed	NH (ppm N)	Total N (ppm)	% sample removed	NH (ppm N)	Total N (ppm)	% sample removed	NH (ppm N)	Total N (ppm)	% sample removed	NH (ppm N)	Total N (ppm)
NCRUDE 85+	855	1621	>5.4	-	-	5.4	233 (2.67)*	664 (1.44)	3.0	333 (1.57)	778 (0.92)	2.1	429 (0.99)	921 (0.76)
UNCOR w coker as oil	592	2017	15.5	-	-	9.1	115 (4.15)	1018 (0.98)	4.7	184 (2.21)	1199 (0.68)	3.0	255 (1.32)	1302 (0.55)
PL ATB	166	380	3.5	0	142	2.5	14 (10.86)	161 (1.36)	1.5	28 (4.93)	197 (0.93)	1.0	39 (3.25)	216 (0.76)

Partition ratios, k_{z_i}, are shown in brackets, where: $k_{z_i} = \frac{C^E_{z_i}}{C^R_{z_i}} = \frac{\text{nitrogen content of the } z_i \text{ compound type in the extractant}}{\text{nitrogen content of the } z_i \text{ component type in the raffinate}}$

TABLE 9

Two Stage Extractions with Dimethylsulfoxide Containing Water

Sample	15% H_2O in DMSO			20% H_2O in DMSO			
	% sample removed	Raffinate NH (ppm N)	Raffinate Total N (ppm N)	% sample removed	Raffinate NH (ppm N)	Raffinate Total N (ppm N)	Extract NH (ppm N)
SYNCRUDE 385+	1.8 (1.3)*	489 (0.75)**	914 (0.77)	0.9 (0.5)	618 (0.38)	1034 (0.57)	22 600
SUNCOR raw coker gas oil	2.5 (1.5)*	286 (1.07)	1244 (0.62)	1.3 (0.9)	390 (0.52)	1409 (0.43)	14 400
IPL ATB	0.8 (0.4)*	54 (2.07)	212 (0.79)	0.4 (0.3)	75 (1.21)	252 (0.51)	18 000

* Yields of 1st stage extractions are shown in brackets

** Other numbers in the brackets are values of the distribution ratios.

TABLE 10

Denitrogenation of Syncrude 385°C+ Fraction

Treatment	N Content (ppm)
Untreated sample	1621
1st stage extraction with 2% H_2O in DMSO	664
2nd stage extraction with 2% of 5N HCl in DMSO	344
1st stage extraction with 6% H_2O in DMSO	778
2nd stage extraction with 6% of 5N HCl in DMSO	460
1st stage extraction with 10% H_2O in DMSO	921
2nd stage extraction with 10% of 5N HCl in DMSO	669

TABLE 11

2nd Stage Extractions with DMSO Containing Acid. Total Nitrogen Contents, ppm

Treatment		1st Stage Raffinate of SSC ATB	1st Stage Raffinate of IPL ATB	1st Stage Raffinate SUC GO
Untreated Raffinate		811	158	1304
Extractions with acid, % in DMSO	6 of 5N H_3PO_4	507	136	1286
	6 of 5N Acetic Acid	537	117	917
	6 of 10N Acetic Acid	536	144	1124
	6 of 1N H_2SO_4	466	91	723
	6 of 5N H_2SO_4	428	71	646
	6 of 10N H_2SO_4	403 (2.90)	67 (1.66)	471 (4.90)
	6 of 12N H_2SO_4	613	-	696

* Extraction yields shown in brackets, wt%.

TABLE 12

Extractions with Alternate Solvents

	1st Stage Extraction with DMF/H_2O (9:1)			2nd Stage Extraction with DMSO/H_2O (94:6)		
	Yield	N, ppm		Yield	N, ppm	
Sample	Wt%	Raffinate	Extract	Wt%	Raffinate	Extract
SSC ATB	4.54	920	12,000	3.08	612	5,892
IPL ATB	2.66	192	6,844	1.01	112	3,628
SUC Gas Oil	7.54	1321	10,802	5.54	1007	5,299

TABLE 13

Extractions with Alternate Solvents

Sample	1st Stage Extraction with NMP/H_2O (9:1)			2nd Stage Extraction with DMSO/H_2O (94:6)		
	Yield	N, ppm		Yield	N, ppm	
	Wt%	Raffinate	Extract	Wt%	Raffinate	Extract
SSC ATB	10.26	628	17,915	6.66	492	6,123
IPL ATB	4.60	140	15,895	3.22	110	4,659
SUC Gas Oil	No phase separation			-	-	-

TABLE 14

Analyses of Polar Extracts

	Extract obtained with DMSO/H_2O (94:6)			Nonbasic Fraction* of the Extract		
Origin	Yield	Total N, ppm	NH (N ppm)	Yield	Total N, ppm	NH (N ppm)
SSC ATB	3.56	15,624	11,300	69.1	11,241	12,200
IPL ATB	1.96	8,746	6,800	77.7	7,392	6,800
SUC GO	5.25	11,712	7,730	61.8	10,170	6,600

* Obtained by dissolving the extract in toluene, extracting basic components with DMSO containing 6% of 10N H_2SO_4 and then distilling off toluene from the raffinate.

TABLE 14A

Preconcentration* of Polars from Non Basic Fraction of the Extract

Extract Origin	Sub-Fraction	Total N (ppm)	NH (ppm N)
SSC ATB	polar	20 769	19 671
	nonpolar	438	-
IPL ATB	polar	23 409	20 667
	nonpolar	591	-
SUC GO	polar	17 143	10 541
	nonpolar	119	-

* Sequential liquid chromatography on clay column. The nonpolar material was eluted with hexane. The polar species were incompletely recovered using 8:2 diethylether/methanol as eluent.

TABLE 15

Supercritical Fluid Extractions With Acetone

Feed	Weight of Sample, g	Volume of Acetone, cc	Temperature (°C)	Appr. Equilibrium Pressure, psi	Successive Extract Fractions, g				Total Amount of Sample Extracted, %
					1	2	3	4	
AB ATB	202.0	956	290	1500	13.1	8.8	5.4	3.8	15.7
AB VTB	201.8	960	290	1500	9.5	5.7	2.9	1.3	9.6
LHO ATB	202.0	956	290	1550	15.1	10.4	7.2	4.8	18.6
LHO VTB	190.7	790	310	1600	8.1	4.6	2.2	1.4	8.6
IPL VTB	198.7	960	290	1600	7.4 (1.7)*	3.8 (0.53)	2.9 (0.28)	1.3 (0.07)	7.7 (1.3)
SSC ATB	200.0	960	290	1500	19.9	18.6	12.6	8.3	29.7

* precipated wax contents are shown in brackets

TABLE 16

Supercritical Fluid Extractions with Acetic Acid

Feed	Weight of Sample, g	Volume of Acetic Acid, cc	Temperature (°C)	Appr. Equilibrium Pressure, psi	Successive Extract Fractions, g				Total Amount of Sample Extracted, %
					1	2	3	4	
LHO ATB	199.3	916	336	1200	16.1	5.4	3.5	2.9	14.0
LHO VTB	197.5	916	333	1050	11.8	29.6	2.8	2.4	23.6
IPL VTB	201.3	916	337	1250	23.7	9.6	5.5	3.5	21.0

TABLE 17

Supercritical Fluid Extractions with Methanol

Feed	Weight of Sample, g	Volume of Methanol, cc	Temperature (°C)	Appr. Equilibrium Pressure, psi	Successive Extract Fractions, g				Total Amount of Sample Extracted, %
					1	2	3	4	
LHO ATB	171.6	911	265	1700	9.0	6.5	4.0	2.6	12.9
LHO VTB	149.4	811	265	1600	0.6	0.4	0.2	0.2	0.9

TABLE 18

Extractions with Sulfur Dioxide

Experiment No.	Feed	Sample, g	SO_2, g	Temperature (°C)	Appr. Equilibrium Pressure, psi	Successive Extract Fractions, g		
						1	2	3
1	AB ATB	101.2	647	221	2600	4.8	3.7	2.1
2	LHO VTB	102.5	475.6	270	2400	no extracts taken due to burst disc destruction		
3	LHO ATB	100.0	350	173	1120	1.937	-	-
4	SSC ATB	101.6	465	163	1050	0.125	-	-
5	SSC GO	100.8	400	174	1040	0.17	-	-
6	SSC ATB	113	600	70	170	0.0284	-	-
7	SSC ATB	113	591.8	101	170	0.1366	-	-
8	IPL ATB	100.2	470	176	1250	0.992	-	-
9	LHO ATB	102.2	520	201	1800	1.4	-	-
10	SSC ATB	132.1	515	189	1510	1.2346	-	-

TABLE 19

Summary of Conditions and Yields for Supercritical Water Extractions

Feed	Samples, g	H_2O, g	Temperature (°C)	Approx. Equilibrium Pressure, psi	Extract, g
SSC ATB	100.0	324.6	384	3600	12.4 in 41.9 g of H_2O
IPL ATB	102.7	325.3	385	3850	14.5 in 46.5 g of H_2O
LHO ATB	100.0	325.0	387	3600	8.9 in 58.2 g of H_2O
AB ATB	105.0	341.0	382	3500	5.9 in 58.3 g of H_2O
SUC GO	108.0	334.7	384	3900	14.9 in 48.8 g of H_2O
LHO VTB	111.9	337.4	385	3700	3.8 in 56.1 g of H_2O
IPL VTB	104.7	335.0	389	4000	2.3 in 70.6 g of H_2O
AB VTB	101.5	325.0	386	3600	4.1 in 61.5 g of H_2O

TABLE 20

Analyses of Extracts and Raffinates from Acetone Extractions

Feed	Sample	Total N (ppm)	NH (ppm N)	V (ppm)	Ni (ppm)
AB ATB	Extract	1880	51	5.1	2.9
	Raffinate			178	87
LHO ATB	Extract	1210	39	34.6	14.3
	Raffinate			157	102
IPL VTB	Extract	2540	83	9	11
	Raffinate			135	31
SSC ATB	Extract	1330	86		
	Raffinate				
LHO VTB	Extract	1996		40.2	221
	Raffinate			195	102
AB VTB	Extract	2300	48	81.5	22.4
	Raffinate			252	121

TABLE 21

Analyses of Extracts and Raffinates from Methanol and Acetic Acid Extractions

Feed	Solvent	Sample	Total N (ppm)	V (ppm)	Ni (ppm)
LHO ATB	Acetic Acid	Extract	2585	24.1	599
		Raffinate		240	619
LHO VTB	Acetic Acid	Extract	3380	53	1273
		Raffinate		123	891
IPL VTB	Acetic Acid	Extract	3152		
		Raffinate		27	278
LHO ATB	Methanol	Extract	1328		
		Raffinate		173	82
LHO VTB	Methanol	Extract			
		Raffinate		107	2179

TABLE 22

Analyses of Extracts and Raffinates from Sulfur Dioxide Extractions

Experiment No.	Feed	Sample	NH (ppm N)	Total N (ppm)	V (ppm)	Ni (ppm)
1	AB ATB	Extract	370		52	56
3	LHO ATB	Extract	352			
		Raffinate	164		172.3	82.3
4	SSC ATB	Extract	646	868		
		Raffinate	800	1233		
5	SUC GO	Extract	126			
		Raffinate	357			
6	IPL ATB	Extract		225		
		Raffinate		279		
9	LHO ATB	Extract		758		
10	SSC ATB	Extract		1095		

TABLE 23

Analyses of Extracts and Raffinates Obtained Using Water Under Supercritical Conditions

Experiment No.	Feed	Sample	Total N (ppm)	NH (ppm N)	V (ppm)	Ni (ppm)
1	SSC ATB	Extract	1114	750	8	<1
		Raffinate	1263	830	15	<1
2	IPL ATB	Extract	326	160	-	-
		Raffinate	368	170	-	-
3	LHO ATB	Extract	1633	300	780	69
		Raffinate	5028	620	100	250
4	AB ATB	Extract	3020	492	1300	43
		Raffinate	8966	583	145	243
5	SUC GO	Extract	1667	438	-	-
		Raffinate	1720	520	-	-
6	LHO VTB	Extract	4597	465	382	80
		Raffinate	5948	569	181	350
7	IPL VTB	Extract	3258	854	953	14
		Raffinate	3746	806	22	28
8	AB VTB	Extract	3679	728	371	142
		Raffinate	6348	800	160	-

TABLE 24

MAT Product Yields for SCC ATB Raffinates

Feed:	SSC ATB Untreated	Raffinate (2% H_2O in DMSO)	Raffinate (6% H_2O in DMSO)	Raffinate (10% H_2O in DMSO)	Raffinate (15% H_2O in DMSO) Two Stages	Raffinate (6% H_2O in DMSO) Water Stripped	Raffinate (9:1 NMP/H_2O
Test:	MAT 518	MAT 531	MAT 410	LC-6	LC-22	LC-26	LC-2
Mass Balance, wt%	101.0	101.43	96.2	102.3	104.9	105.8	102.3
Temperature, °C	489	490	490	491	490	490	490
C/O, g/g	3.61	3.31	3.95	4.10	4.19	4.18	4.33
Product Yields, wt%							
H_2	0.14	0.08	0.12	0.07	0.10	0.10	0.12
CH_4	0.37	0.66	0.68	0.94	0.51	0.32	0.40
$<C_2$	1.35	1.73	2.01	2.30	1.44	1.08	1.32
ΣC_3	4.19	4.01	4.36	4.06	3.62	3.26	4.43
ΣC_4	7.60	7.16	7.29	7.19	6.47	6.38	8.57
ΣC_5	2.59	4.00	3.72	3.75	4.55	4.42	5.02
C_5+ gasoline	39.2	43.2	42.8	40.3	42.4	44.1	43.6
C_6+ gasoline	36.6	39.2	39.0	36.6	37.8	39.7	38.6
LCO	22.8	21.7	22.4	21.5	22.3	22.1	22.1
DO	21.4	18.4	17.1	20.6	19.5	19.0	16.3
Coke	3.46	3.75	4.11	3.97	4.28	4.09	3.54
Conversion	55.8	59.9	60.5	57.9	58.2	58.9	61.5
Coke/Conversion	0.0620	0.0626	0.0679	0.0686	0.0735	0.0694	0.0576
C_6+ Gasoline/ Conversion	0.656	0.654	0.645	0.632	0.649	0.674	0.628
Coke/(C/O)	0.958		1.041	0.968	1.021	0.978	0.817

TABLE 25

MAT Product Yields for SCC ATB 2nd Stage
Raffinates (Extractions with DMSO Containing Acid

Feed:	SSC ATB Untreated	Raffinate 2% H_2O in DMSO 2% HCl* in DMSO	Raffinate 6% H_2O in DMSO 6% 10N H_2SO_4 in DMSO	Raffinate 10% H_2O in DMSO 10% HCl* in DMSO	Raffinate 10% H_2O in DMSO 10% HCl* in DMSO Water Stripped
Test:	MAT 518	MAT 588	LC-9	MAT 587	LC-3
Mass Balance, wt%	101.0	101.4	105.0	102.0	100.4
Temperature, °C	489	491	491	489	489
C/O, g/g	3.61	3.72	4.45	4.28	3.84
Product Yields, wt%					
H_2	0.14	0.13	0.09	0.13	0.11
CH_4	0.37	0.41	0.34	0.44	0.38
$<C_2$	1.35	1.40	1.13	1.45	1.37
ΣC_3	4.19	4.34	3.98	4.30	4.12
ΣC_4	7.60	7.77	7.48	7.86	7.54
ΣC_5	2.59	4.34	4.20	5.11	4.03
C_5^+ gasoline	39.2	44.3	43.8	42.6	42.7
C_6^+ gasoline	36.6	40.0	39.6	37.5	38.7
LCO	22.8	21.9	22.7	22.3	22.0
DO	21.4	16.6	17.0	17.4	18.8
Coke	3.46	3.64	3.82	4.15	3.44
Conversion	55.8	61.5	60.2	60.4	59.2
Coke/Conversion	0.0620	0.0592	0.0634	0.0689	0.0581
C_6^+ Gasoline/ Conversion	0.656	0.650	0.658	0.622	0.654
Coke/(C/O)	0.958	0.979	0.858	0.971	0.896

* 5N HCl

TABLE 26

MAT Product Yields for SCC ATB Raffinates Containing Added Nitrogen Compounds

Feed:	SSC ATB Untreated	Raffinate (6% H_2O in DMSO, Water Stripped) + 13 H-Dibenzo(a,i) Carbazole	Raffinate (6% H_2O in DMSO, Water Stripped) + Acridine	Raffinate (6% H_2O in DMSO, Water Stripped) + 7,8-Benzo quinoline	Raffinate Two Stages Water Stripped + 13 H-Dibenzo(a,i) Carbazole and Acridine	Raffinate (2% H_2O in DMSO, Water Stripped) + nonbasics	Raffinate (2% H_2O in DMSO, Water Stripped) + 7,8-Benzo quinoline	Reconstituted SSC ATB
Test:	MAT 518	LC-10	LC-12	LC-14	LC-13	MAT 584	MAT 585	MAT 491
Mass Balance, wt%	101.0	100.8	101.1	102.1	100.7	101.0	102.0	99.1
Temperature, °C	489	490	490	490	491	488	489	490
C/O, g/g	3.61	4.24	4.23	3.92	4.40	3.84	3.76	4.13
Product Yields, wt%								
H_2	0.14	0.12	0.23	0.17	0.13	0.10	0.15	0.13
CH_4	0.37	0.40	0.36	0.29	0.32	0.48	0.38	0.42
$<C_2$	1.35	1.22	1.30	1.04	1.96	1.38	1.19	1.39
ΣC_3	4.19	3.98	3.66	2.84	3.33	3.20	2.68	3.97
ΣC_4	7.60	7.19	6.43	5.13	5.56	5.48	4.76	7.71
ΣC_5	2.59	3.54	3.30	3.40	3.17	3.10	2.64	4.93
C_5^+ gasoline	39.2	39.1	37.9	36.1	39.5	35.1	32.6	39.7
C_6^+ gasoline	36.6	35.5	34.6	32.7	36.4	32.0	29.9	34.7
LCO	22.8	22.6	29.5	22.0	20.5	22.6	21.9	21.1
DO	21.4	21.9	16.8	29.8	25.1	28.6	33.8	22.3
Coke	3.46	4.07	4.36	3.08	4.00	3.64	3.11	3.84
Conversion	55.8	55.5	53.7	48.3	54.4	48.9	44.3	56.6
Coke/Conversion	0.0620	0.0733	0.0812	0.0638	0.0735	0.0745	0.0703	0.0678
C_6^+ Gasoline/ Conversion	0.656	0.6396	0.6443	0.6770	0.6691	0.655	0.675	0.613
Coke/(C/O)	0.958	0.960	1.031	0.786	0.909	0.949	0.828	

TABLE 27

MAT Product Yields for IPL ATB Raffinates

Feed:	IPL ATB Untreated	Raffinate (6% H_2O in DMSO)	Raffinate (5% H_2O in DMSO, Stripped)	Raffinate (10% H_2O in DMSO)	Raffinate (9:1 NMP/H_2O)	Raffinate (9:1 DMF/H_2O)
Test:	MAT 519	MAT 493	LC-25	MAT 535	LC-1	LC-4
Mass Balance, wt%	102.8	102.7	103.5	101.1	98.5	97.6
Temperature, °C	490	490	490	490	490	490
C/O, g/g	3.51	3.69	4.16	3.87	3.75	3.64
Product Yields, wt%						
H_2	0.08	0.08	0.05	0.08	0.07	0.08
CH_4	0.30	0.40	0.31	0.48	0.31	0.36
ΣC_2	1.14	1.42	1.04	1.49	1.18	1.29
ΣC_3	4.94	5.56	5.19	5.96	6.02	6.23
ΣC_4	10.1	11.6	10.7	11.5	12.68	13.17
ΣC_5	5.51	6.71	5.62	6.09	6.83	7.93
C_5+ gasoline	54.5	58.4	56.2	54.1	55.1	51.9
C_6+ gasoline	49.0	51.7	50.5	48.0	48.3	43.9
LCO	19.2	15.7	17.7	17.3	16.7	17.1
DO	7.42	4.79	6.95	6.89	6.48	8.26
Coke	2.69	2.45	2.22	2.69	1.84	2.08
Conversion	73.4	79.5	75.3	75.8	76.8	74.7
Coke/Conversion	0.0366	0.0308	0.0295	0.0355	0.0240	0.0278
C_6+ Gasoline/ Conversion	0.668	0.650	0.671	0.633	0.629	0.588
Coke/(C/O)	0.766	0.664	0.534	0.695	0.491	0.571

TABLE 28

MAT Product Yields for SUC GO Raffinates

Feed:	SUC GO Untreated	Raffinate Pure DMSO	Raffinate 2% H_2O in DMSO	Raffinate 10% H_2O in DMSO	Raffinate 5% H_2O in DMSO 6% $10NH_2SO_4$ in DMSO
Test:	MAT 409	MAT 411	MAT 533	MAT 534	LC-24
Mass Balance, wt%	98.6	101.0	100.4	98.2	99.8
Temperature, °C	491	490	490	490	489
C/O, g/g	4.11	4.09	3.87	4.05	4.14
Product Yields, wt%					
H_2	0.10	0.10	0.09	0.09	0.08
CH_4	0.52	0.47	0.59	0.55	0.45
$<C_2$	2.75	2.62	2.51	2.66	2.69
ΣC_3	3.96	3.91	4.11	4.01	4.74
ΣC_4	6.17	6.74	6.48	6.30	7.91
ΣC_5	3.41	4.50	3.32	4.14	4.31
C_5^+ gasoline	34.4	38.0	35.2	30.8	40.6
C_6^+ gasoline	31.0	33.5	31.9	26.7	36.3
LCO	31.8	28.6	31.3	31.4	27.5
DO	17.5	16.2	16.2	20.6	12.6
Coke	3.44	4.00	4.18	4.13	3.88
Conversion	50.7	55.3	52.5	48.0	59.9
Coke/Conversion	0.0679	0.0723	0.0796	0.0860	0.0648
C_6^+ Gasoline/ Conversion	0.611	0.606	0.608	0.556	0.606
Coke/(C/O)	0.837	0.978	1.080	1.020	0.937

FIGURES

Figure 1 — Schematic Diagram of the Apparatus for Supercritical Fluid Extractions

Figure 2 — Schematic Diagram of the Apparatus for Microactivity Testing

Figure 3 — Chromatograms of SSC ATB Extracts:
(A) untreated SSC ATB;
(B) acetone extract;
(C) nitromethane extract;
(D) DMSO/H_2O (96:4) extract

Samples were 50 µg. Eluent composition was CCl_4/DMSO (99.97:0.03) 0 min, (99:1) 13 min.

Figure 4 — Chromatograms of IPL ATB Extracts:
(A) DMSO/H_2O (96:4) extract;
(B) nitromethane extract;
(C) acetone extract.

Samples were 50 µg. Eluent composition was CCl_4/DMSO (99.97:0.03) 0 min, (99:1) 13 min.

Figure 5 — Chromatograms of IPL VTB Extracts:
(A) standards: (1) coronene, (2) acridine, (3) carbazole, (4) 1-naphthol, (5) anthracene-9-carboxylic acid;
(B) acetone extract;
(C) nitromethane extract;
(D) DMSO/H_2O (96:4) extract.

Samples were 50 µg. Eluent composition was CCl_4/DMSO (99.97:0.03) 0 min, gradient exponent 5 (99:1 to 50:50) 18 min.

Figure 6 — High Resolution Mass Spectrometry of Extracts. Distillation of Compound Classes: 1) cycloparaffins, 2) monoaromatics, 3) diaromatics, 4) triaromatics, 5) tetraaromatics, 6) pentaaromatics, 7) polyaromatics.

Figure 7 — Infrared Spectra of SSC ATB and its DMSO/H_2O (96:4) Raffinate.

FIGURES Continued

Figure 8 Selectivity Factor vs. % of H_2O in DMSO.

Figure 9 Effect of Water Content on the Denitrogenation Coefficient.

Figure 10 Effect of Water Content on the Removal of NH Constituents.

Figure 11 Denitrogenation with DMSO containing H_2SO_4.

Figure 12 MAT Conversion for SSC ATB Raffinates.
Raffinates:
1) (2:98) H_2O/DMSO
2) (6:94) H_2O/DMSO
3) (10:90) H_2O/DMSO
4) 2nd stage (15:85) H_2O/DMSO
5) (6:94) H_2O/DMSO water stripped
6) (9:1) NMP/H_2O water stripped

Figure 13 MAT conversion for SSC ATB Raffinates Obtained by Two Stage Extractions.
First stage - DMSO containing water
Second stage - DMSO containing acid
Raffinates:
1) (6:94) H_2O/DMSO, (2:98) 5N HCl/DMSO water stripped;
2) (6:94) H_2O/DMSO, (6:94) 10N H_2SO_4/DMSO water stripped;
3) (10:90) H_2O/DMSO, (10:90) 5N HCl/DMSO;
4) water stripped raffinate (3)

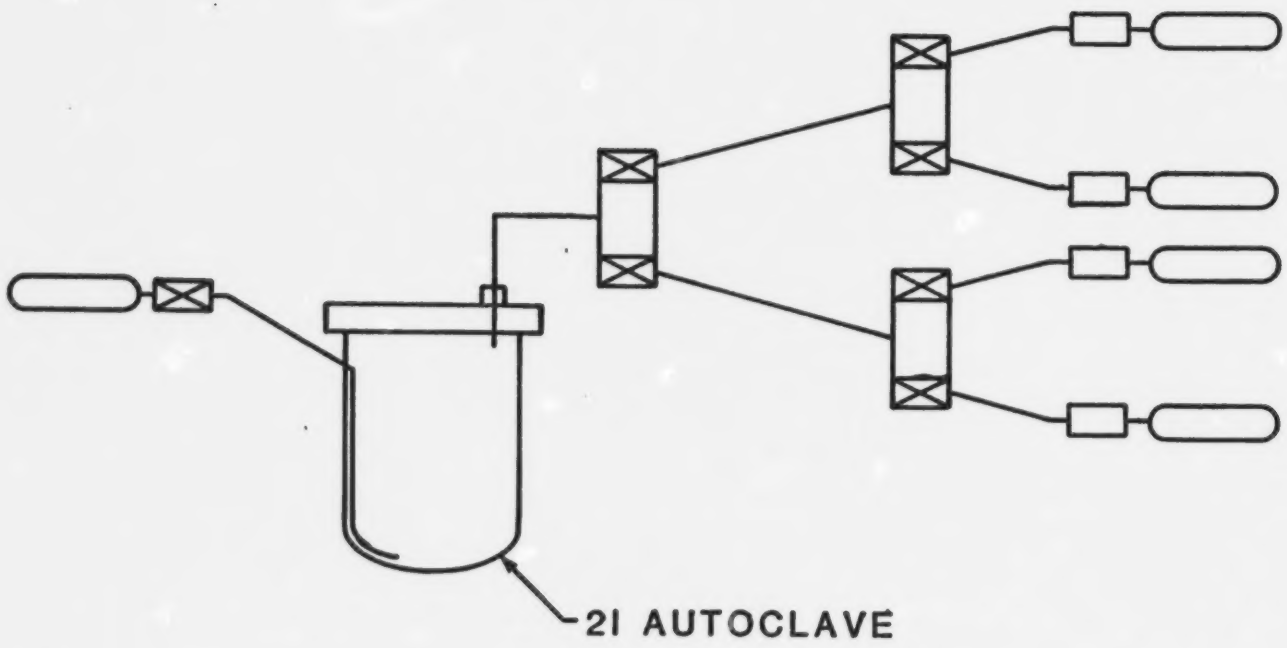
Figure 14 MAT Conversion of SSC ATB Raffinates Spiked with Nitrogen Compounds.
(1) reconstituted SSC ATB; (2-5) (6:94) H_2O/DMSO raffinates spiked with 13D-Dibenzo(a,i)carbazole (675 ppm) - No. 2; acridine (675 ppm) - No. 3; 7,8-Denzoquinoline (675 ppm) - No. 4; (5) (6:94) H_2O/DMSO, (6:94) 10N H_2SO_4/DMSO raffinate spiked with 13H-Dibenzocarbazole (675 ppm) and acridine (430 ppm); (6,7) (2:98) H_2O/DMSO raffinates spiked with 7,8-Benzoquinoline (957 ppm) - No. 6; nonbasic nitrogen components (957 ppm) from the (2:98) H_2O/DMSO extract - No. 7.

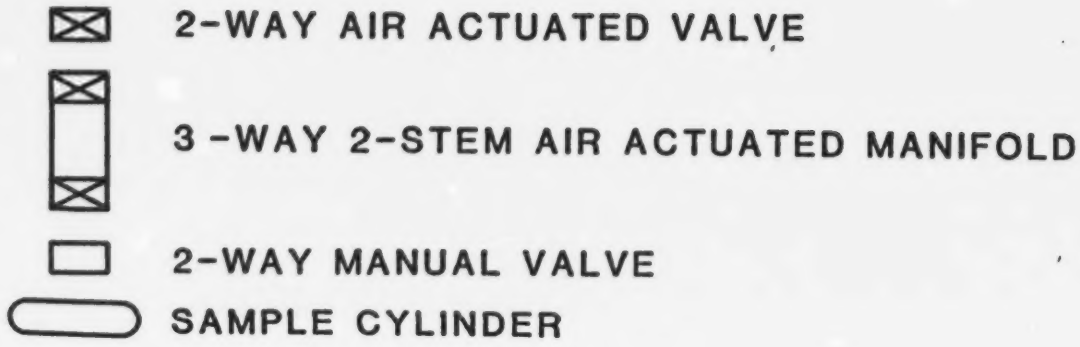
FIGURES Continued

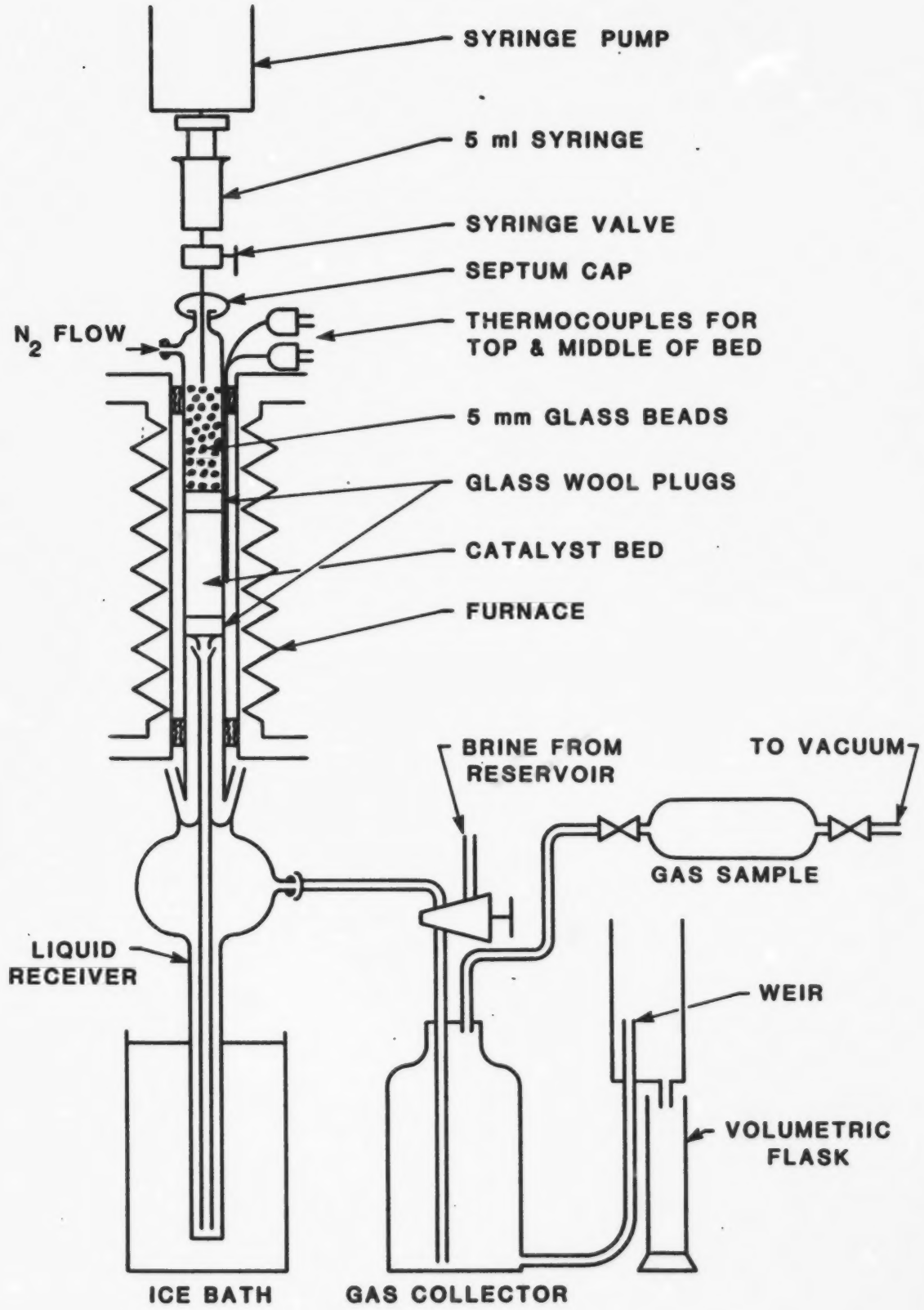
Figure 15 MAT Conversion of IPL ATB (1-5) and SUC GO (1A, 2A) Raffinates

Raffinates:
1) (6:94) H_2O/DMSO
2) (6:94) H_2O/DMSO
3) (10:90) H_2O/DMSO
4) (9:1) NMP/H_2O
5) (9:1) DMF/H_2O
1A) pure DMSO
2A) (6:94) H_2O/DMSO, (6:94) 10N H_2SO_4/DMSO, water stripped

FIGURE 1


2l AUTOCLAVE


2-WAY AIR ACTUATED VALVE
3 -WAY 2-STEM AIR ACTUATED MANIFOLD
2-WAY MANUAL VALVE
SAMPLE CYLINDER



A SCHEMATIC DIAGRAM OF THE MICROACTIVITY TEST APPARATUS

FIGURE 2

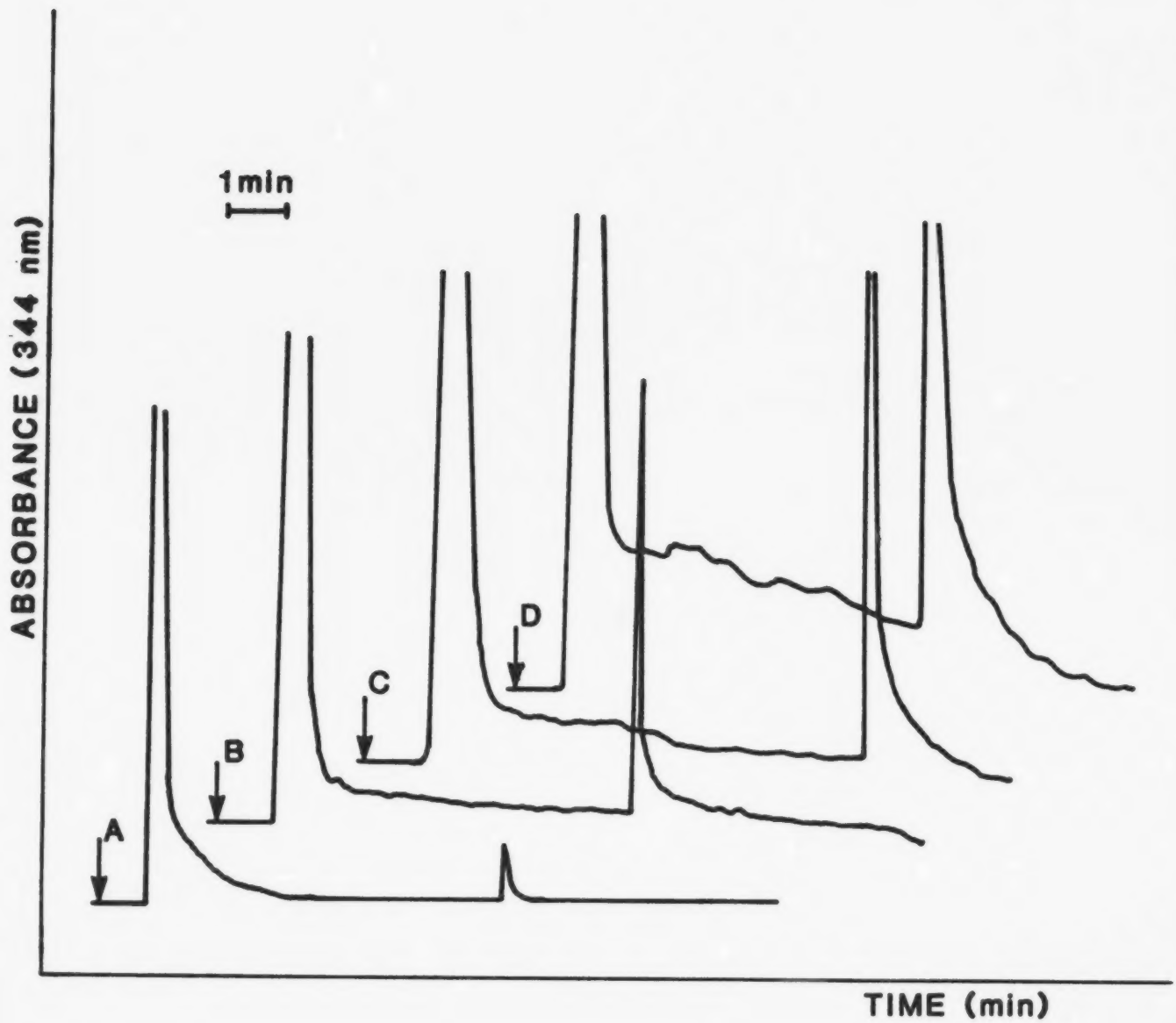


FIGURE 3

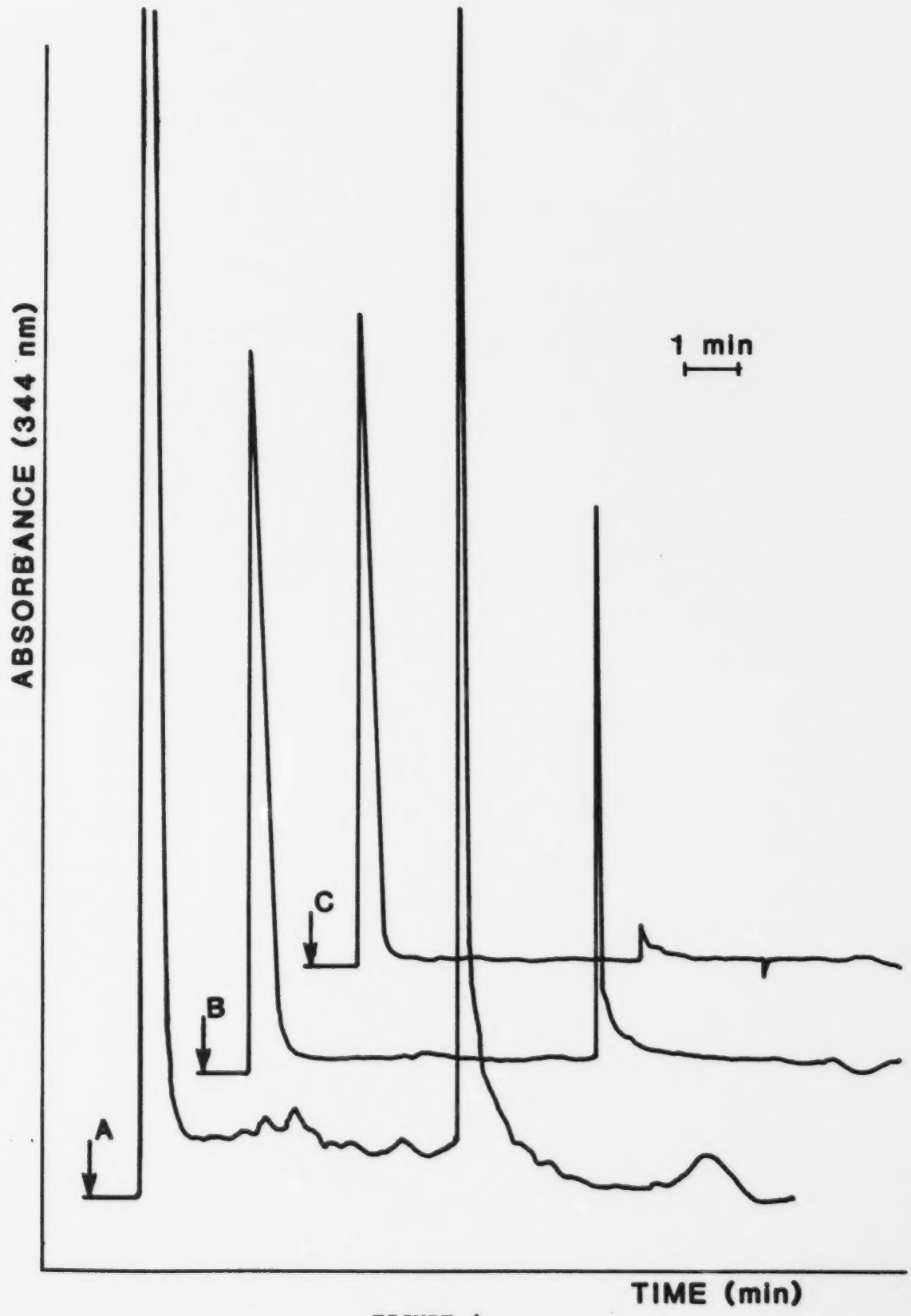


FIGURE 4

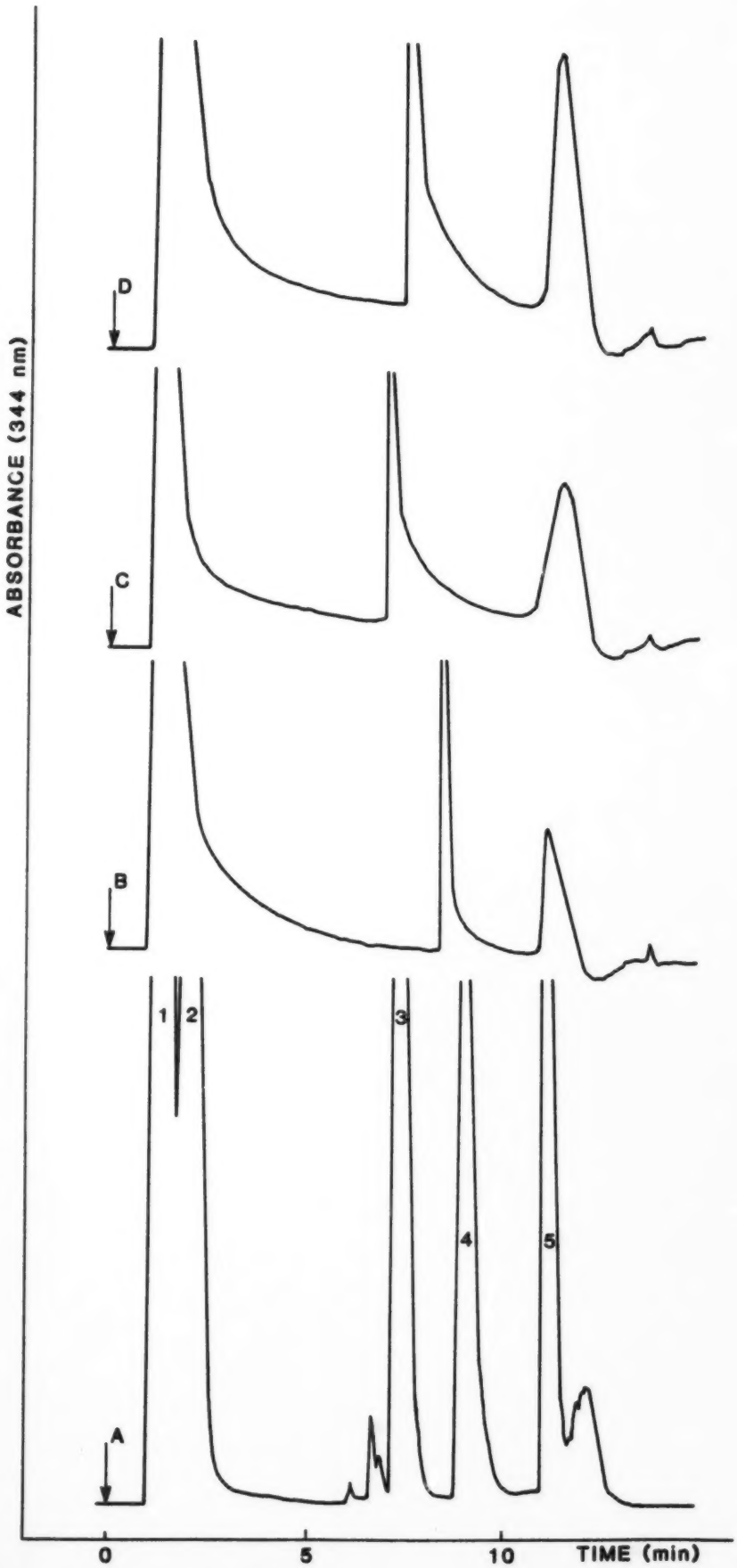


FIGURE 5

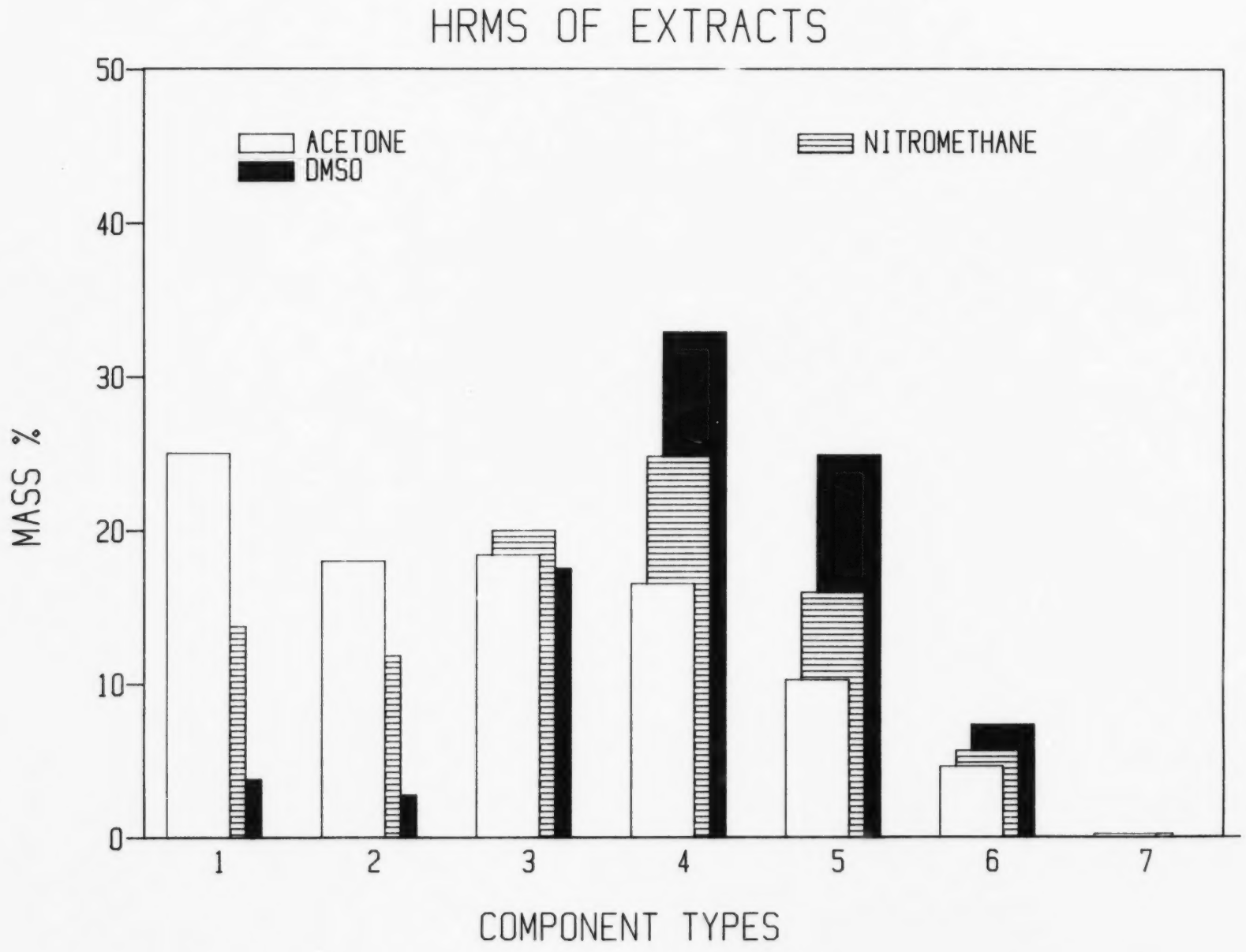

HRMS OF EXTRACTS
ACETONE
DMSO
NITROMETHANE
MASS %
50
40
30
20
10
0
1
2
3
4
5
6
7
COMPONENT TYPES

FIGURE 6

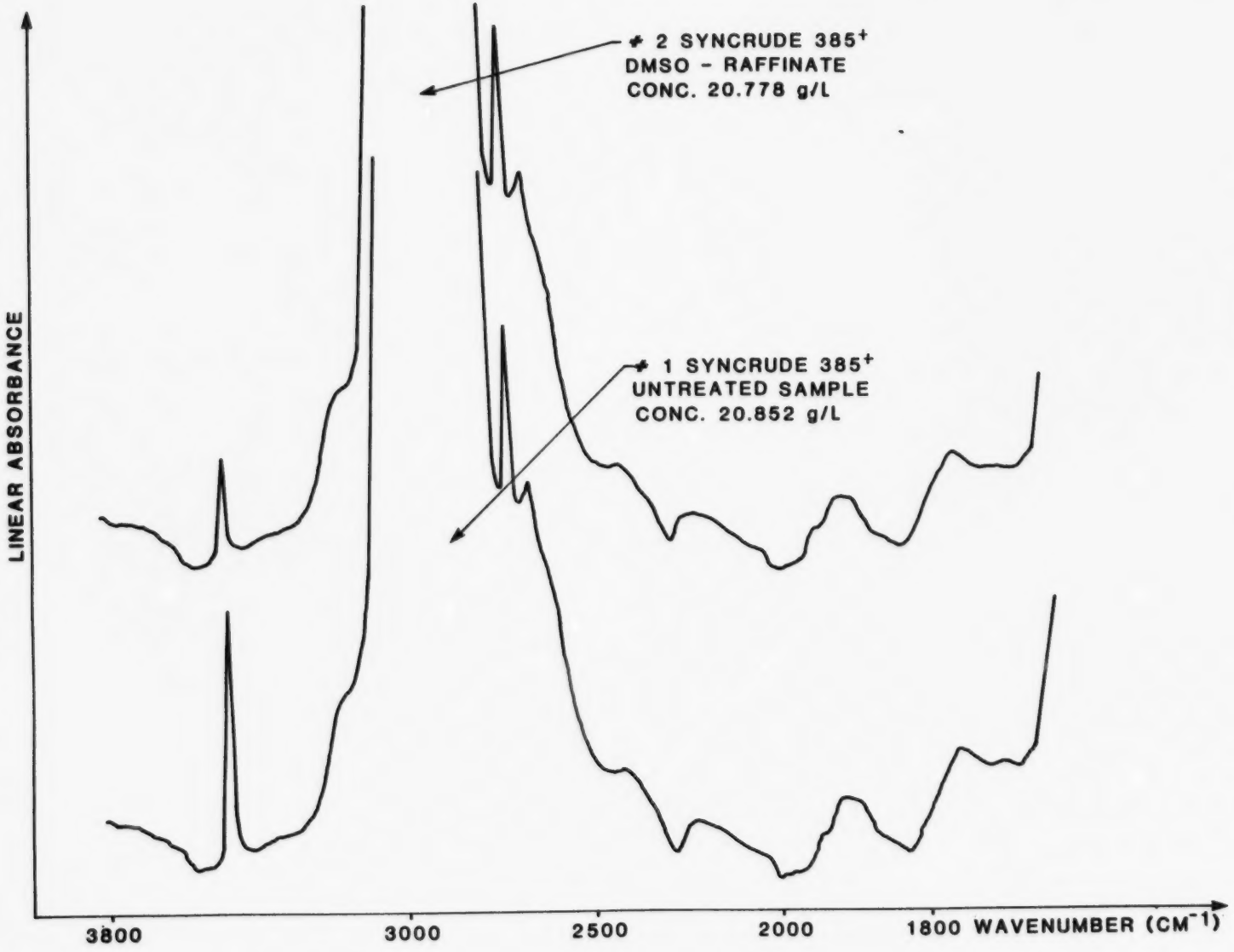

LINEAR ABSORBANCE
2 SYNCRUDE 385+
DMSO - RAFFINATE
CONC. 20.778 g/l
1 SYNCRUDE 385+
UNTREATED SAMPLE
CONC. 20.852 g/l
3800
3000
2500
2000
1800 WAVENUMBER (CM-1)

FIGURE 7

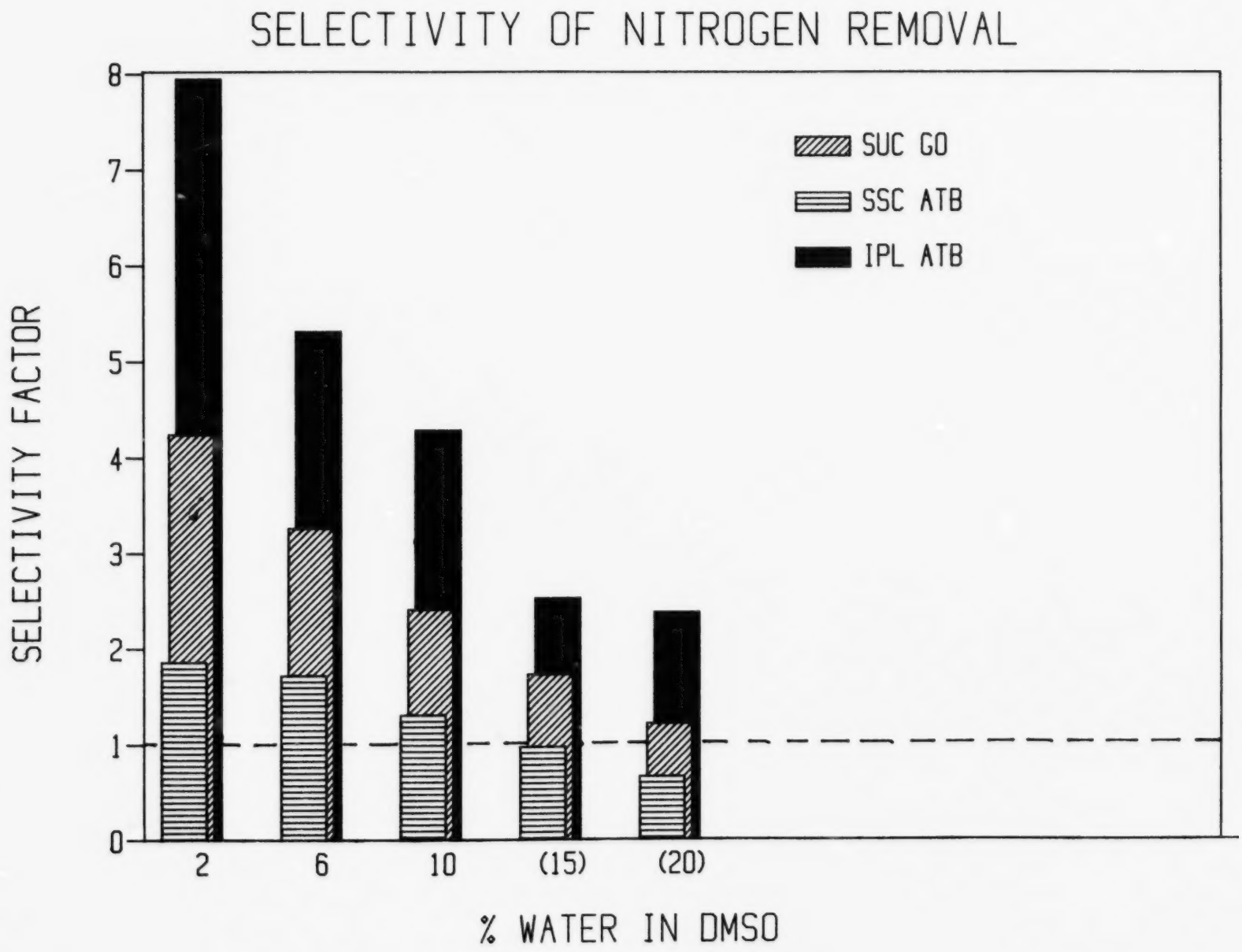

SELECTIVITY OF NITROGEN REMOVAL
SELECTIVITY FACTOR
0
1
2
3
4
5
6
7
8
SUC GO
SSC ATB
IPL ATB
2
6
10
(15)
(20)
% WATER IN DMSO

FIGURE 8

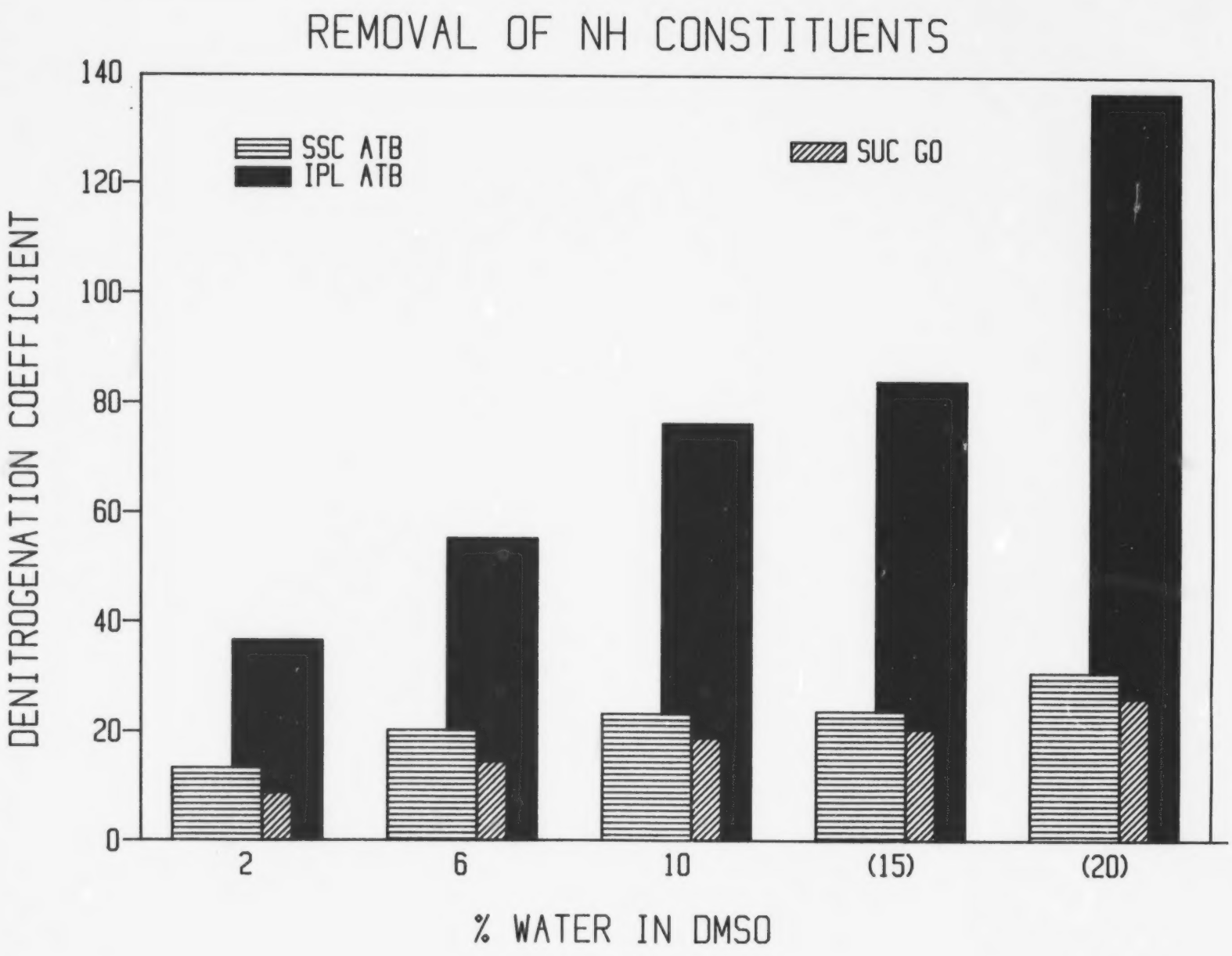

REMOVAL OF NH CONSTITUENTS
SSC ATB
IPL ATB
SUC GO
DENITROGENATION COEFFICIENT
140
120
100
80
60
40
20
0
2
6
10
(15)
(20)
% WATER IN DMSO

FIGURE 10

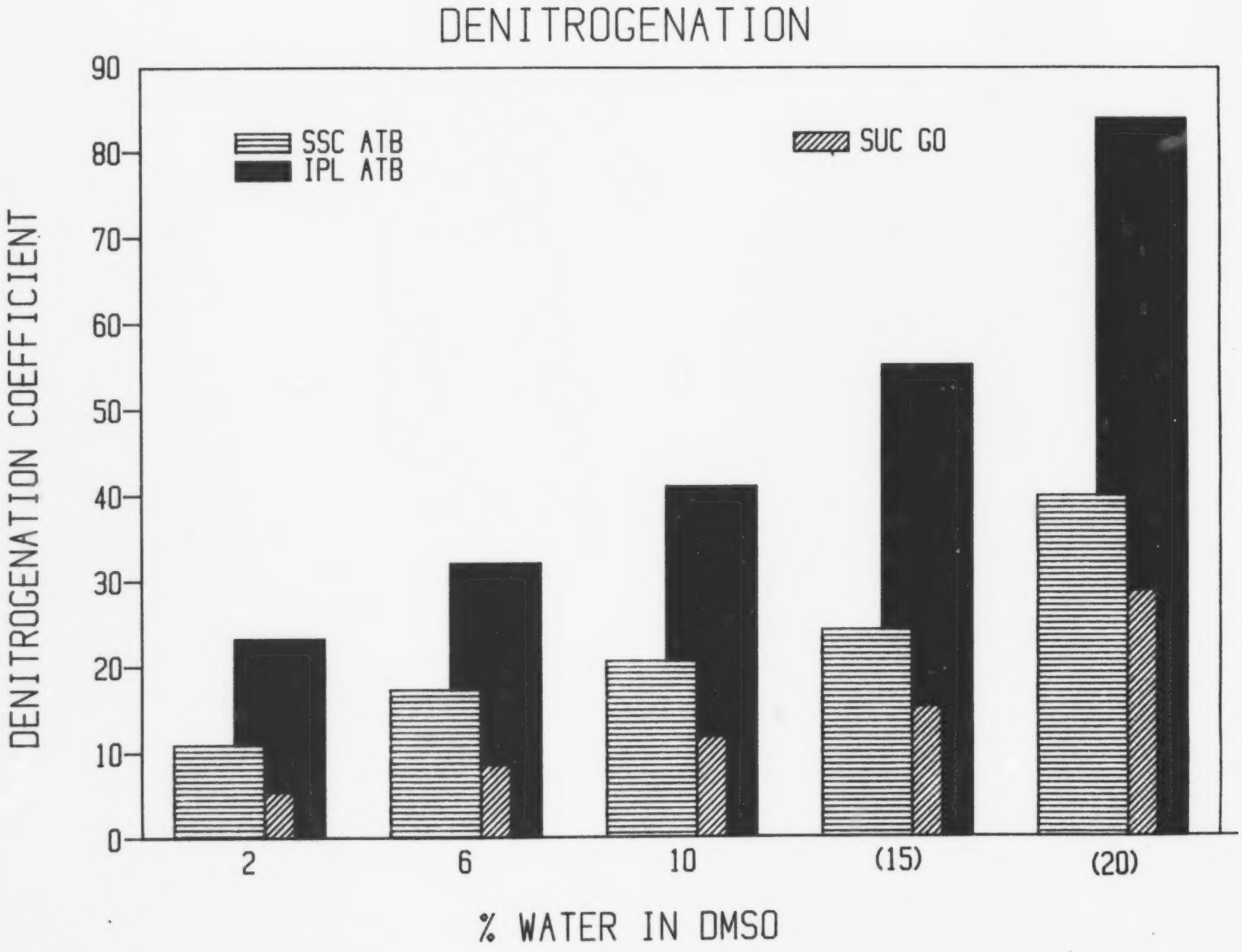

DENITROGENATION
DENITROGENATION COEFFICIENT
90
80
70
60
50
40
30
20
10
0
SSC ATB
IPL ATB
SUC GO
2
6
10
(15)
(20)
% WATER IN DMSO

FIGURE 9

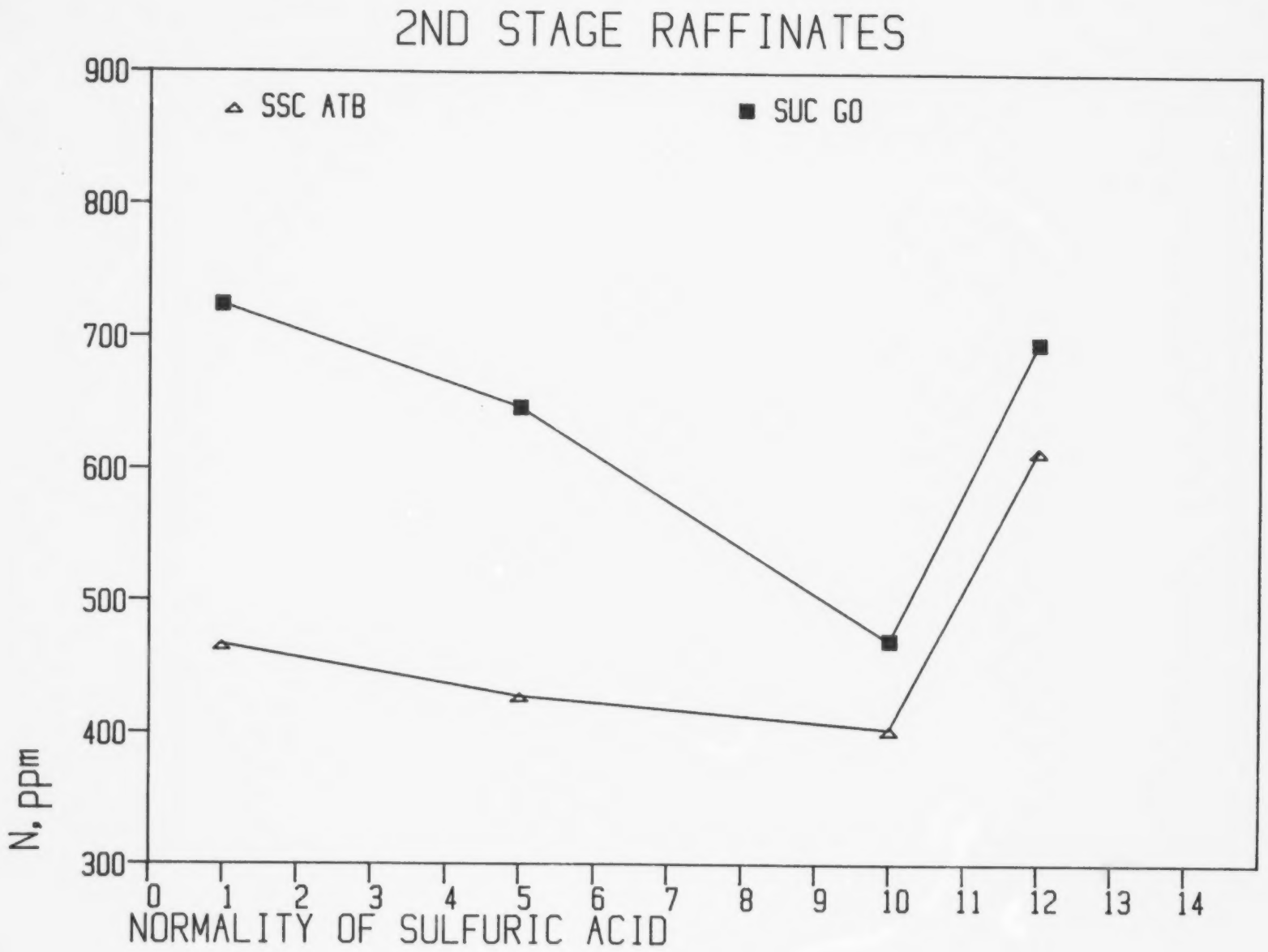

2ND STAGE RAFFINATES
SSC ATB
SUC GO
900
800
700
600
500
400
300
N, ppm
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14
NORMALITY OF SULFURIC ACID

FIGURE 11

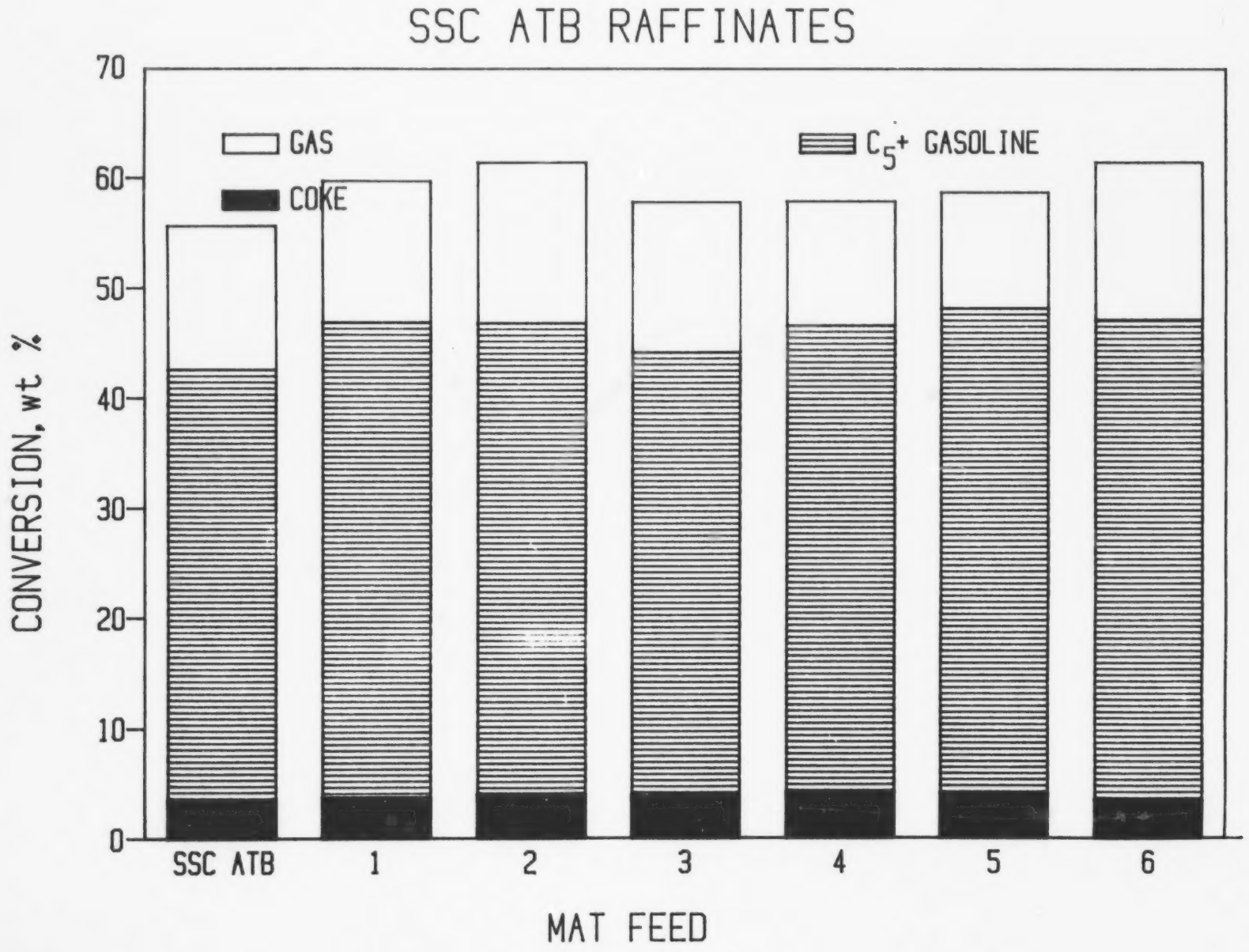

SSC ATB RAFFINATES
70
60
50
40
30
20
10
0
GAS
COKE
C_5+ GASOLINE
CONVERSION, wt %
SSC ATB
1
2
3
4
5
6
MAT FEED

FIGURE 12

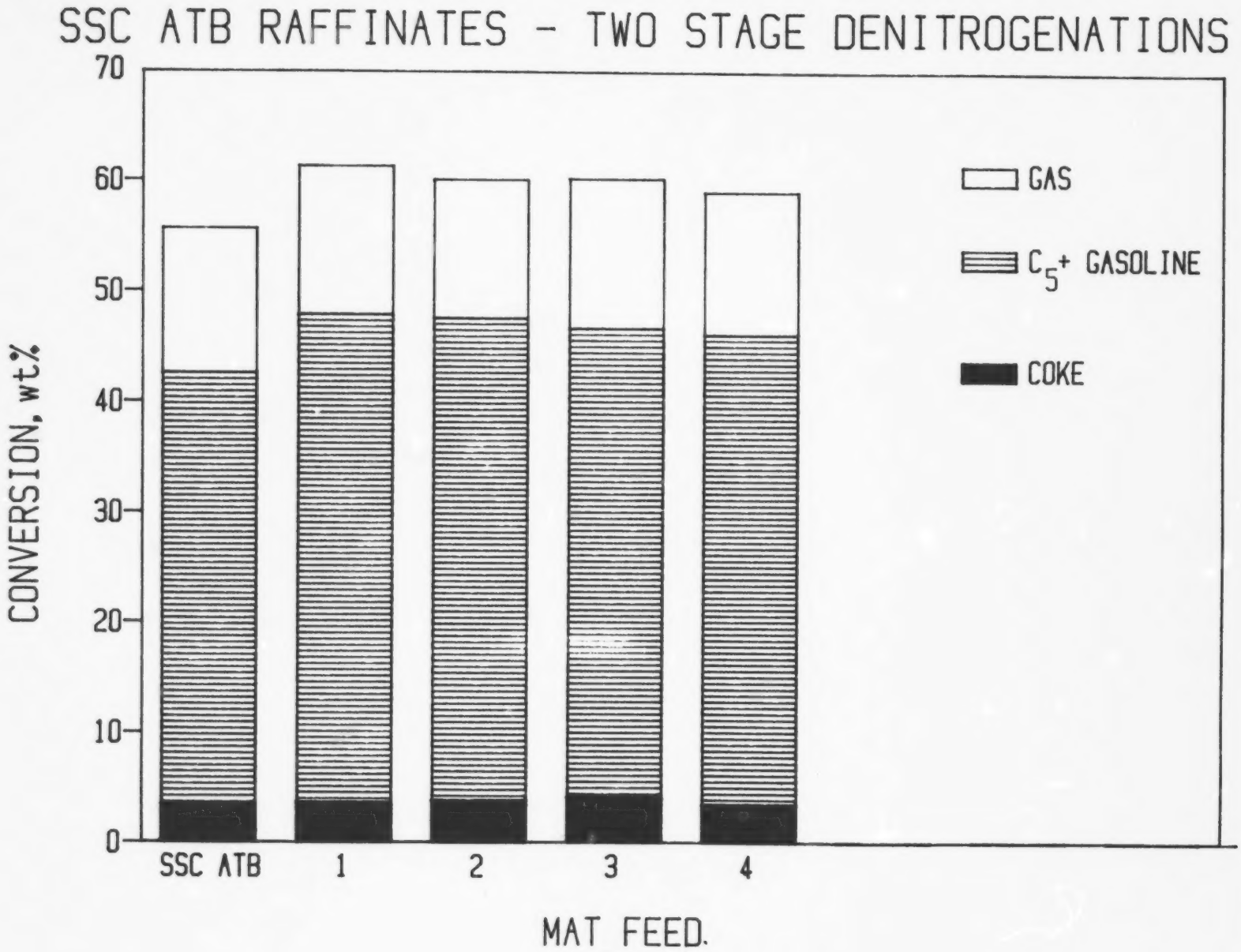

SSC ATB RAFFINATES - TWO STAGE DENITROGENATIONS
CONVERSION, wt%
70
60
50
40
30
20
10
0
SSC ATB
1
2
3
4
MAT FEED.
GAS
C5+ GASOLINE
COKE

FIGURE 13

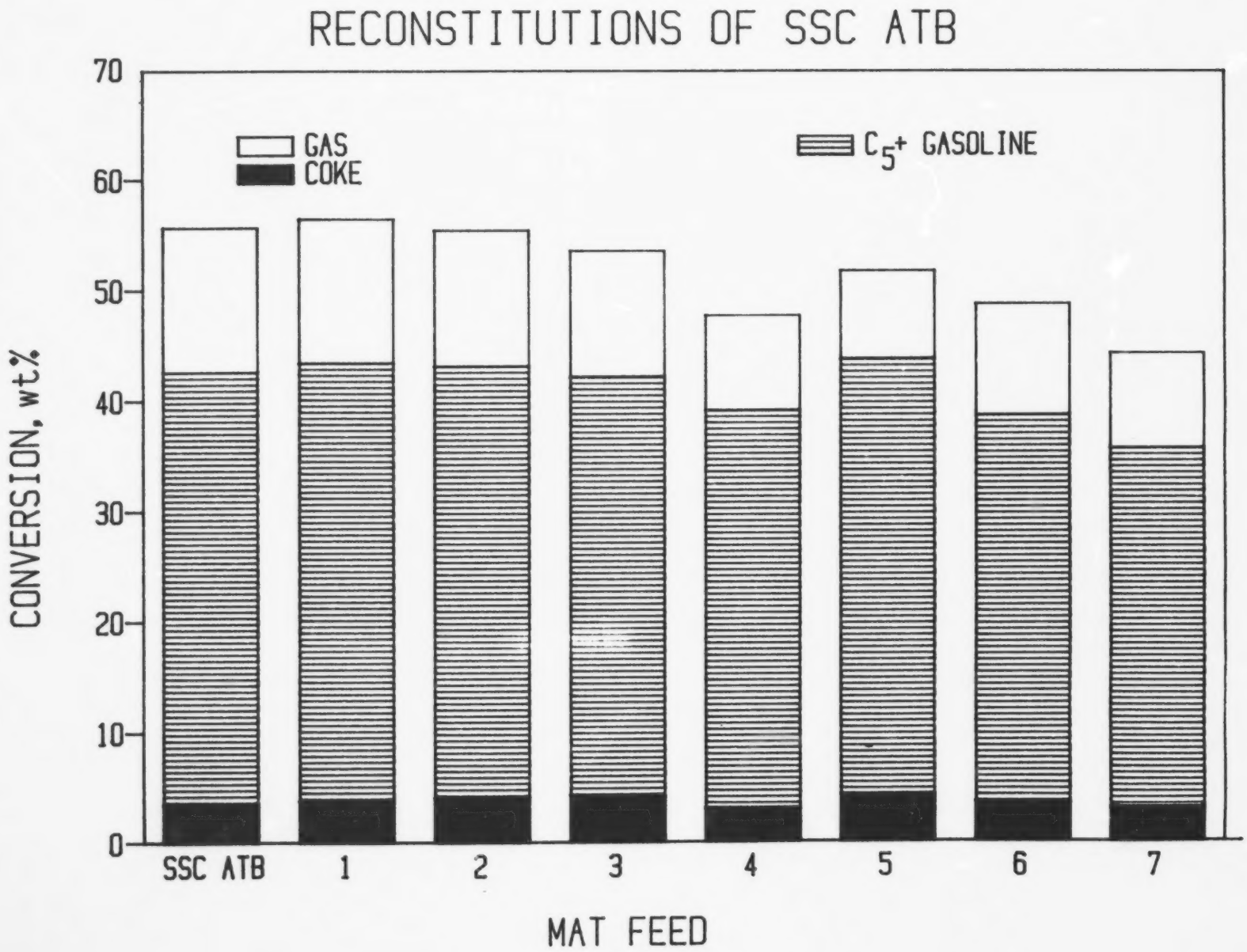

RECONSTITUTIONS OF SSC ATB
70
60
50
40
30
20
10
0
GAS
COKE
C5+ GASOLINE
CONVERSION, wt%
SSC ATB
1
2
3
4
5
6
7
MAT FEED

FIGURE 14

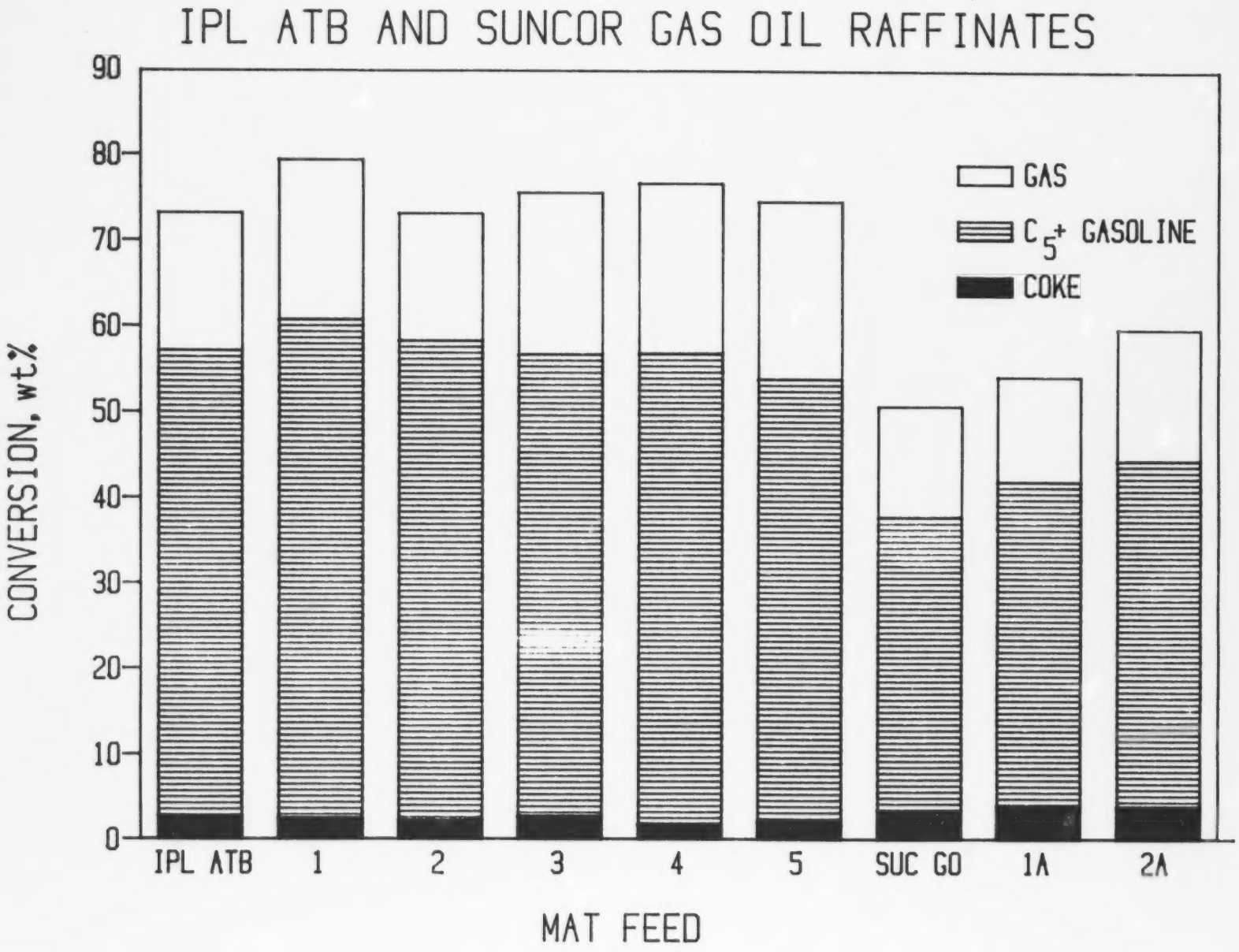

IPL ATB AND SUNCOR GAS OIL RAFFINATES
CONVERSION, wt%
90
80
70
60
50
40
30
20
10
0
GAS
C5+ GASOLINE
COKE
IPL ATB
1
2
3
4
5
SUC GO
1A
2A
MAT FEED

FIGURE 15

APPENDIX 1

1. Procedure for Autoclave Assembling and Pressure Testing - No Reactants

1.1 Inspect sealing surfaces.
1.2 Install a bursting disc (2000 psi).
1.3 Attach the autoclave head and torque bolts (75 psi).
1.4 Connect a nitrogen cylinder and pressurize the autoclave appr. to 100 psi. Check for leaks.
1.5 Check the sampling system for leaks at 100 psi.
1.6 Repeat 1.4 and 1.5 at 1000 psi.

2. Experimental Procedure - Acetone Solvent

2.1 Charge the autoclave (60% maximum capacity).
2.2 Assemble the autoclave.
2.3 Purge with nitrogen for 10 seconds to avoid solvent losses (through top).
2.4 Pressure test with nitrogen as in 1.4 but at maximum pressure 1200 psi.
2.5 Leave nitrogen in the sampling system (slight positive pressure).
2.6 Install the stirrer drive belt, place heater in position, install thermocouples and attach water cooling to stirrer
2.7 Turn on heater.
2.8 Start the stirrer at 150°C at minimum speed of 800 rpm.
2.9 Stir 10 minutes at 290°C.
2.10 Allow 5 minutes for disengaging phases with the stopped stirrer.
2.11 Collect sample of the fluid by air-actuating valves No. 5 and No. 1. Allow the dropping pressure to stabilize shut off air supply to the actuators and repeat 2.8 and 2.9 three more times using, successively, valves in pairs as follows: No. 5 and No. 2, No. 6 and No. 3 and No. 6 and No. 4.

2.12 Collect sample of the feed by acuating valve connected to the drip-leg tube. Shut off air supply.

2.13 Turn off the heater. Allow 15 minutes for monitoring the pressure. If constant or dropping, lower the heater and apply external surface cooling.

2.14 When ambient pressure has been reached, allow the autoclave to vent for at least 30 minutes to evolve any dissolved gases.

2.15 Open and clean the autoclave.

3. Shut-down Option

Open the pressure release valve when pressure approaches 1800 psi and turn off heater.